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THE OSMOTIC PRESSURE AND FREEZING-POINTS OF SOLUTIONS OF CANE-SUGAR.[1]

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Nearly three years ago the authors published[2] under the title "The Preparation of Cells for the Measurement of High Osmotic Pressures" an account of the results which they had obtained with the electrolytically deposited copper ferrocyanide membrane, previously described[3] by Morse and Horn. Pressures of over 30 atmospheres had been obtained and it was supposed by the authors that, having solved in a satisfactory manner the problem of depositing the membranes and having overcome, in a measure, the difficulties connected with the assembling of the different parts of the cell, they could proceed, without further delay, to the measurement of osmotic pressure. But it soon appeared that a third problem, the most difficult of all, remained to be dealt with, *i. e.*, the problem of the *porous wall*. The porous cups in which the high pressures referred to had been obtained were a part of a lot of 100, which were made

[1] This work has been carried on with the aid of grants from the Carnegie Institution.

[2] THIS JOURNAL, 28, 1.

[3] *Ibid.*, 26, 80.

for the authors at a pottery in a neighboring city. Out of this number 25 or 30 had been found to answer the requirements moderately well and it was not doubted that others equally good, or better, could be readily procured. In this we were greatly mistaken, for among the nearly 500 cells which were subsequently made for us at various potteries *not one* was found suitable for the measurement of osmotic pressure. An entire year was spent in procuring and testing porous cells from different sources, but to very little purpose, except to convince us that the problem of producing the cells must be worked out in the laboratory rather than at the pottery. The potters, in attempting to produce, by their methods, porous vessels which they conceived to be suitable for our purposes, unwittingly introduced or magnified defects from which the earliest cells were fairly free. Our later experience has shown us that a different result was not to be expected, inasmuch as the production of the correct texture of porous wall for the measurement of osmotic pressure involves a resort to methods not ordinarily practiced by the potters.

Having failed to procure cells of the required character, we proceeded to make a microscopic study of thin sections of a considerable number of those which had been previously tested with membranes, selecting for the purpose cells which could be classified as fairly good, bad and indifferent. It was hoped, by this means, to discover the peculiarities of texture which determine the suitability of a porous wall for experimental work and, having found them, that methods might be devised which would insure the reproduction, at will, of the essential qualities. The work along these lines is far from finished and the results are, therefore, not ready for publication. We have already succeeded, however, in producing, in the laboratory, a few cells of almost ideal excellence and with these the measurements of pressure here recorded were made.

In order to provide others, as well as ourselves, with a safe basis for a criticism of the procedure and for a judgment of the weight to be assigned to the results, also to avoid unnecessary repetition in future communications, we shall describe, in some detail, the apparatus which has been employed

and the methods which have been followed, beginning with the manometer.

The form of the manometers which have been used in these experiments is shown in Figs. I. and II. Two such instruments have been employed, which will be designated as No. 3 or No. 4 whenever there is occasion for mentioning one or the other specifically.

Originally, *i. e.*, after the first filling, No. 3 had a length of air column amounting to about 413 mm. under atmospheric pressure, at ordinary temperatures, while the length of air column in No. 4, under similar conditions, amounted to about 428 mm. But, since it is necessary from time to time to open and refill the instruments, the quantity of the enclosed air is subject to some variations. The diameter of the bore is about 0.5 mm. Greater accuracy of measurement could, of course, be secured by using longer manometers with larger volumes of enclosed air, but development in this direction is limited in various ways. It is rarely possible to find tubes, of any great length, which are sufficiently straight throughout for use as manometers. Again, an objection to long manometers is the greater difficulty which is experienced with them in avoiding accidents while securing them in their places in the cells. The manipulation at this point is difficult, even under the most favorable conditions. But the principal consideration which renders the use of large volumes of air inadvisable is the obvious fact that the contraction, under pressure, of the gas in the manometer is attended by an equivalent increase in the volume of the contents of the cell. The absolute volume of this contraction should not, of course, be so great as to result in a sensible dilution of the solution.

The air column, under high pressures, is very short, amounting, in the manometers used by us, to only about 16 or 17 mm. when the pressures to be measured reach 25 atmospheres. The accurate calibration of the instruments is, therefore, a matter of great importance. The method of calibration which we have used is similar, in principle, to that which is employed for eudiometers. Fig. II. represents the instrument which we constructed for the purpose.

A steel screw, with a light, rather long, wooden handle at its lower end *a*, serves to adjust the short thread of mercury at *h*, in any desired position in the manometer tube, the thread being separated from the mercury below by a short column of air; *b* is a cup of hard rubber, which is turned to the proper form on the lathe, bored and threaded for the screw *a*. In cutting the thread upon the screw great pains are taken to secure an exact fit to the thread in the cup, in order to avoid leakage of mercury. The glass tube *i* is fixed in the rubber cup by means of litharge-glycerine cement, which is shown at *d*. The tube is enlarged at *c* to prevent slipping and contracted at *e* in order to hold the rubber stopper *f* more firmly in its place. A still further provision against leakage of mercury is made by slightly oiling the upper end of the screw and allowing cement to solidify about the thread. Finally, the whole thread is lubricated with a rather stiff paste, made by fusing together rubber, vaseline and paraffin.

The manometer has etched upon it three lines of reference, two of which, *g*, are located in the same horizontal plane—one below the bulb and the other opposite to it on the ascending limb. The third line, which is not shown in the figure, is located near the top of the manometer. The instrument should not be otherwise graduated, owing to the interference of lines with readings by the telescope.

Near the open end of the manometer the tube is enlarged to a bulb, as shown at *j* in Fig. I. This feature of the instrument is indispensable, since without it, it is impossible to keep the manometer in the cell when more than very moderate pressures are developed. Formerly we employed, in its place, a cone-shaped mass of shellac, which was attached to the glass, but this, though it rendered good service for a time, was liable, after a few experiments, to become detached in consequence of the penetration of liquid between the glass and the shellac.

The bulb in the descending limb of the manometer, which serves as a reservoir for the mercury, is made as large as is consistent with the required strength of the wall. The purpose of this is two-fold: first, the solution is much less likely

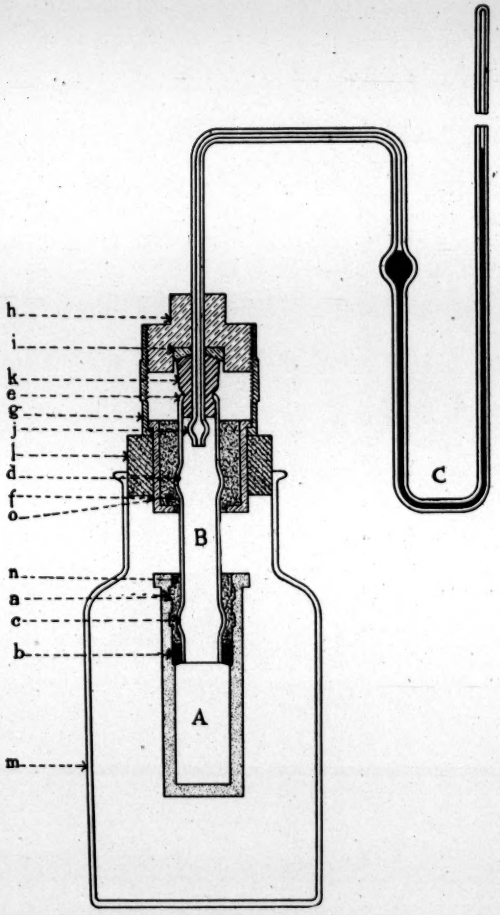

Fig. I.

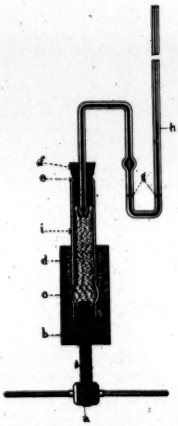

Fig. II.

to get past the mercury into the air space during the somewhat strenuous manipulation which is necessary when the manometer is inserted in the cell; and second, the level of the mercury in the bulb (which must be knowu when a reading is made) is subject to such slight variations in a large bulb that one determination of its height above the line of reference serves for all the readings which are made during any single experiment. An ample reservoir for the mercury is quite essential, since the whole apparatus, when in use, is buried in hair to insure an even temperature of the contents of the cell.

The most trying and critical operation connected with the setting up of a cell is the insertion of the stopper carrying the manometer. The pressure which must be brought upon the stopper to force it into its place is considerable, and this cannot be relaxed, even in a slight degree, from the beginning to the end without danger that a portion of the enclosed air will pass the bend in the tube and escape into the bulb. This difficulty can be remedied in great part, and will be hereafter, by blowing another bulb near the bottom of the ascending limb of the manometer.

Before proceeding to describe the method of calibrating the manometer, it may not be superfluous to explain that all observations are made with a telescope, which is provided with a micrometer eye-piece and that all readings are taken from a standard meter, which is mounted in a vertical position at a short distance from the cathetometer. The meter scale and the cathetometer rest upon foundations which do not come in contact, at any point, either with the floors or walls of the laboratory and the stability of the instruments, which is thus secured, is entirely satisfactory. The cells, while under observation, and the manometer while undergoing calibration, rest upon the same foundation as the meter scale. Great care is taken to secure an exactly vertical position for the cathetometer, the standard scale and the manometer. The first is adjusted until the vertical spider line of the telescope will follow thin plumb-lines in planes at right angles to one another, while the correct positions for the other two are found with the aid of the telescope and plumb-lines.

The calibration of the manometer is carried out in the following manner: The tube *i* is filled with mercury and the manometer (with its upper end still open) is fixed in its place as shown in Fig. II. The method of introducing the stopper *f* into the tube *i*, when the latter is full of liquid, will be explained later, in connection with the manipulation of the cell. Having brought the apparatus to a vertical position with the aid of adjustable clamps attached to a stiff steel standard, which is firmly fixed in the foundation, the screw is turned upwards until the mercury fills the manometer to within about 1 mm. of the top. A drop of mercury is then placed upon the upper open end of the tube and the screw turned in the other direction. A short thread of mercury (*h*, Fig. II.) is thus introduced, which is separated from the unbroken column below by a shorter column of air. The thread of mercury is made to descend in the tube until its lower end is exactly opposite the line of reference. The distance between its two ends is then determined with the aid of the telescope and the standard scale.

Having found the length of the space filled by the fixed column of mercury just above the line of reference, the thread is pushed upwards until its lower end occupies exactly the previous position of the upper end, when another set of readings is made. In this way the thread is placed end to end and the length of the space occupied after each setting is determined until the top of the tube is reached.

In order to use conveniently the data thus obtained all the observations are reduced to a calibration unit and the results are plotted in the form of a curve. The calibration data for the instruments Nos. 3 and 4, which were the ones used in these experiments, are given in the following tables. The first column in each table gives the actual readings on the graduated scale. The second column gives the differences between the successive readings, *i. e.*, the length of the mercury thread in the different parts of the tube. The readings on the meter, which would have been obtained if the zero of the graduated scale had coincided with that of the manometer, are given in the third column.

Table I.—Data for Calibration of Manometer No. 3.

I. Readings upward on scale.	II. Differences.	III. Readings on meter calculated from the zero-point.	IV. Products of number of settings by mean space filled.	V. Correction values.
918.77	13.92	13.92	13.858	—0.06
904.85	14.08	28.00	27.716	—0.28
890.77	14.06	42.06	41.574	—0.49
876.71	14.08	56.14	55.432	—0.71
862.63	14.13	70.27	69.290	—0.98
848.50	14.12	84.39	83.148	—1.24
834.38	14.07	98.46	97.006	—1.45
820.31	14.07	112.53	110.864	—1.67
806.24	14.11	126.64	124.722	—1.92
792.13	14.02	140.66	138.58	—2.08
778.11	14.03	154.69	152.438	—2.25
764.08	13.96	168.65	166.296	—2.35
750.12	13.92	182.57	180.154	—2.42
736.20	13.81	196.38	194.012	—2.37
722.39	13.75	210.13	207.870	—2.26
708.64	13.68	223.81	221.728	—2.08
794.96	13.71	237.52	235.586	—1.93
681.25	13.63	251.15	249.444	—1.71
667.62	13.65	264.80	263.302	—1.50
653.97	13.67	278.47	277.160	—1.31
640.30	13.63	292.10	291.018	—1.08
626.67	13.73	305.83	304.876	—0.95
612.94	13.75	319.58	318.734	—0.85
599.19	13.75	333.33	332.592	—0.74
585.44	13.71	347.04	346.450	—0.59
571.73	13.75	360.70	360.308	—0.39
557.98	13.81	374.60	374.166	—0.43
544.17	13.76	388.36	388.024	—0.34
530.41	13.78	402.14	401.882	—0.26
516.63	13.77	415.91	415.740	—0.17
502.86	13.76	429.67	429.598	—0.07
489.10	13.89	443.56	443.456	—0.10
475.21	13.75	457.31	457.314	+0.004
461.46				

Table II.—Data for Calibration of Manometer No. 4.

I. Readings upward on scale.	II. Differences.	III. Readings on meter calculated from the zero-point.	IV. Product of number of settings by mean space filled.	V. Correction values.
901.69	12.55	12.55	12.186	—0.364
889.14	12.42	24.97	24.372	—0.598
876.72	12.45	37.42	36.558	—0.862
864.27	12.50	49.92	48.744	—1.176
851.77	12.34	62.26	60.930	—1.330
839.43	12.52	74.78	73.116	—1.664
826.91	12.34	87.12	85.302	—1.818
814.57	12.51	99.63	97.488	—2.142
802.06	12.40	112.03	109.674	—2.356
879.66	12.41	124.44	121.860	—2.580
777.25	12.42	136.86	134.046	—2.814
764.83	12.32	149.18	146.232	—2.948
752.51	12.45	161.63	158.418	—3.212
740.06	12.38	174.01	170.604	—3.406
727.68	12.38	186.39	182.790	—3.600
715.30	12.30	198.69	194.976	—3.714
703.00	12.34	211.03	207.162	—3.868
690.66	12.33	223.36	219.348	—4.012
678.33	12.43	235.79	231.534	—4.256
665.90	12.35	248.14	243.720	—4.420
653.55	12.28	260.42	255.906	—4.514
641.27	12.27	272.69	268.092	—4.598
629.00	12.14	284.83	280.278	—4.552
616.86	12.16	296.99	292.464	—4.526
604.70	12.14	309.13	304.650	—4.480
592.56	12.01	321.14	316.836	—4.304
580.55	12.00	333.14	329.022	—4.018
568.55	12.05	345.19	341.208	—3.982
556.50	11.92	357.11	353.394	—3.716
544.58	11.88	368.99	365.580	—3.410
532.70	11.90	380.89	377.766	—3.124
520.80	11.80	392.69	389.952	—3.738
509.00	11.85	404.54	402.138	—2.402
497.15	11.79	416.33	414.324	—2.006
485.36	11.65	427.98	426.510	—1.470
473.71	11.71	439.69	438.696	—0.994
462.00	11.70	451.39	450.882	—0.508
450.30	11.66	463.05	463.068	+0.018
438.64				

Referring to Table I., containing the calibration data for manometer No. 3, it will be observed that in setting the mercury thread 33 times, end to end, a space was covered which, measured on the standard scale, amounted to 457.31 mm. Dividing this number by 33, the number of settings, the average length of the space filled by the fixed amount of mercury is found to be 13.858 mm. The mercury thread was, therefore, regarded as containing 13.858 volume or calibration units. Column IV. gives the multiples of this number corresponding to the several readings in column III. The differences are contained in column V. They are, of course, the corrections which are to be applied at the 33 points in order to convert actual into calibrated or volume readings.

In the same way, the average space filled by the mercury thread was found to be 12.186 mm. in manometer No. 4 and the thread was, therefore, regarded as having a volume of 12.186 calibration units.

The corrections contained in column V. of each table were used as ordinates to plot curves, lines representing the manometers serving as the axes of abscissas.

The coöperation of two persons is necessary in a calibration experiment, one of whom sets the mercury thread while the other directs his movements and makes the readings from the telescope. In order to set the thread correctly, it is quite necessary to tap the tube vigorously and to continue doing so each time until no further movement of the mercury can be observed.

The method here described has the advantage that the calibration of a tube can be carried to any required degree of refinement, since by beginning at other points, above or below the reference line, any desired number of intermediate ordinates may be secured for the correction curve.

To fill a manometer, it is connected at the bottom, by means of a rubber tube, with a reservoir of mercury which can be raised or lowered according as the air is to be expelled from, or drawn into the instrument. At the top it is joined to an apparatus consisting of two connected tubes, one of them con-

taining glass wool upon which has been deposited resublimed phosphorus pentoxide and the other solid potassium hydroxide and calcium chloride, to remove from the air, before it enters the pentoxide tube, carbon dioxide, ammonia and a portion of the water.

At intervals of half an hour, air thus purified is repeatedly drawn into and expelled from the manometer, which is finally closed in the following manner: A disk of sheet platinum is heated to a bright red color, near the center, with the tip of the blow-pipe flame. The heated spot, on the side opposite to the flame, is rubbed with a fragment of manometer tubing until a sufficient quantity of glass, in a thin fluid condition, has accumulated upon the metal. The manometer is then instantly closed by touching its upper end with the liquid glass. Afterwards the glass is rounded off by softening the extreme end of the manometer in the flame, while the air within is under slightly diminished pressure.

The open end of the filled manometer is immersed in mercury and there attached to the arrangement which is to serve as an adjustable reservoir in determining the volume of the enclosed air. This consists of a small rubber tube to which is joined a piece of manometer tubing, having the same bore as the manometer itself. Before connecting with the manometer, the rubber tube and a portion of the glass tube are filled with mercury, care being taken to insure the expulsion of all air from the former.

To determine the quantity of enclosed air, the manometer is fixed in a vertical position before the cathetometer, the level of the mercury in the reservoir tube is adjusted to that of the column within the manometer, pains being taken to ascertain that the relation of the two is not permanently altered by pinching the rubber connecting tube. Finally, the readings in millimeters are converted, with the aid of the calibration curve, into calibration volumes, which are afterwards reduced to their value under standard conditions of temperature and pressure.

When a manometer is closed in the manner here described,

there is some doubt as to the volume which should be assigned to that portion of the bore the form of which is affected by the softening of the glass. Professor Abegg has kindly called our attention to one method of obviating this difficulty—that of displacing the air in the upper end of the manometer with a short column of mercury. The device is, no doubt, an excellent one, but we have been unable to employ it successfully in our manometers. In the few cases where we have tried it, we found that the separation of the necessary thread of mercury involved a roughness of manipulation which appeared to endanger the instrument. Moreover, we were unable to effect a sufficiently complete dislodgment of the air from the space which the mercury should fill.

The form of the interior surface of the tubes, in the region in question, is usually quite uniformly conical or spherical in appearance and we have assumed it to be strictly so in estimating the capacity of the upper ends of our manometers. Nevertheless, whenever it has been necessary to open a manometer for the purpose of refilling it, we have laid aside for further examination the end which was cut off.

After filling a manometer and finding the volume of the enclosed air, the exact distance between the two lines of reference on the vertical limb is ascertained and the capacity of the tube above the upper line is calculated, once for all. In the subsequent work, all readings are referred to one or the other of these lines and it is not necessary to locate, each time an observation is made, what the observer would regard as the proper starting-point at the top after correction for the change in the form of the bore.

The process of preparing the cell for use is so complex that we shall describe the different steps in their order, under the headings 1, 2, 3, etc.

1. The porous cell, designated by A in Fig. I., is mounted on the lathe in a chuck, the construction of which was explained in our earlier communication and, while slowly turning, it is ground internally to a distance from the end equal to somewhat more than a third of its length. The grinding is continued until the shoulder, formed at the bottom of the ground

area, extends entirely around the cell and is of sufficient width to afford an ample support, at all points, for the soapstone ring *b*. Afterwards two channels, one of which is designated in the figure by the letter *a*, are cut into the wall in order to prevent the dislodgment of the cement under pressure. The machine which was constructed for the grinding process is bolted to the tool carriage of the lathe. It carries a carborundum disk which makes about 9,000 revolutions per minute. At this speed the work is quickly accomplished without injury to the cell.

2. The glass tube B, which connects the cell A with the manometer C, should not be unnecessarily large or long. It is, at the best, the weakest part of the entire apparatus, *i. e.*, the part which is most likely to burst under high pressure. It should, therefore, be selected, if possible, from stock which has been thoroughly tested as to the toughness and the enduring qualities of the material. Otherwise one is liable, at a critical moment, to lose the labor of several weeks. The tube is enlarged at *c* and at *d*, where it is afterwards surrounded with cement. Both enlargements are indispensable, for without them the tube will either be pushed out of the cell or through the metal piece *o*. Furthermore, it is contracted at *e* to give a stronger grip upon the rubber stopper *k*.

3. The soapstone ring *b* plays an important rôle in the apparatus and it must be fitted to its place with great care. It is bored and turned on the lathe until it will slip over the end of the glass tube and into the cell. Its lower end is beveled inwards to prevent the lodgment of air.

To make a tight joint between the stone and the glass and to bind the two materials firmly together, the tube, with the ring in place, is inverted, and any space which is left between them is filled with molten shellac. The tube and ring are then placed in an air-bath, in the inverted position, and heated until the shellac is solid at a temperature a little above 100°. The reason for raising the fusing-point of the shellac by distilling out the more volatile matter will be understood when the next step is described.

4. The cement, which is employed to fix the glass tube B and the soapstone ring in their places in the cell, must be effectually protected from any contact either with the solution with which the apparatus is filled or with the water in which it is immersed. For this purpose the lower end of the glass tube, the soapstone ring and the whole of the ground surface within the cell are repeatedly painted with a rather dilute solution of rubber, which is prepared by first fusing pieces of black tubing and then dissolving the product in carbon bisulphide. The liquid is spread as uniformly as possible and, after each application, the wet surfaces are allowed to dry for a time. When a coating of sufficient thickness has been obtained, the soapstone ring, which is now firmly attached to the glass tube, is inserted in the cell and crowded into its place on the shoulder. The last operation is liable to lacerate, more or less, the rubber covering of the cell wall. To repair any damage of this kind and also to insure a tight joint between the clay wall and the soapstone ring, the whole cavity above the latter is again painted with the rubber solution. The apparatus is then placed in an air-bath and maintained at a temperature of 100° until the rubber becomes quite hard, but not brittle. Finally, the space between the cell wall and the glass tube is filled with the usual mixture of lead oxide and glycerine. It is to be noted, in this connection, that the oxide which is prepared in the laboratory, by heating the carbonate, gives much more satisfactory results than are obtained with the commercial litharge. When the cement has hardened—which it should be allowed to do for several days before the cell is used—its upper, exposed surface is also covered with rubber.

We have tried to substitute rings of hard rubber for those of soapstone, but without success. Every cell has cracked in which a ring of the former kind was used, apparently without any other cause than the diversity of the expansion coefficients of the materials.

5. The arrangement by which the stopper and manometer are held in the cell consists of the four brass pieces designated by the letters *o*, *g*, *h* and *i*. The piece *o* is firmly fixed in its place with litharge-glycerine cement, after the completion of

the preparations which have been described under 4. The width of *g*, under the flange, is equal to the greatest diameter of the cell. If, after burning, the width of the cell at the top is found to be somewhat greater than that of *g*, the rim of the former is ground to size while the cell is mounted on the lathe for the purpose of grinding out the interior.

The collar *g* is threaded internally about two-thirds its length from the top and is provided, at the lower end, with an interior flange which locks with the exterior flange of *o*. The surface of the raised, central portion of the outside is milled to provide a firmer hold for the hands.

The nut *h* is threaded externally to fit the interior thread of the collar *g*. At the upper end it is made hexagonal in form, in order that it may be held with a wrench while the stopper is driven into the cell by turning the collar *g*.

In order to obtain satisfactory measurements of osmotic pressure, it is indispensably necessary that all parts of the stopper *k*, which lie outside of the glass tube B, shall be so effectively supported that the rubber cannot, even under the highest pressures, move in any direction except toward the interior of the cell. This is accomplished, in part, by the brass piece *i*, which is concavé at the bottom where it rests upon the stopper. The means by which the sides of the stopper are made rigid will be explained later, in connection with the procedure which is followed in setting up the cell for a measurement of pressure.

Since the holes through *h* and *i* are only a little larger than the manometer which passes through them, they must be placed upon the latter before the bulb *j* is blown and they cannot, thereafter, be removed.

The glass bottle *m* contains the water in which the cell is immersed. The cork ring *l*, which holds the cell in its place in the bottle, is split in a vertical direction to provide for the free passage of air.

6. The removal of the air from the porous wall of the cell, previous to the deposition of the membrane, has been effected, from the beginning of our work, by means of "electrical endosmose" and we have, as yet, discovered no reason for changing our procedure at this stage.

A narrow glass tube, with a side branch for the overflow, is passed through a stopper which is inserted in the cell at *e*. Through the vertical limb of this tube a stout platinum wire, which serves as a cathode, is lowered into the cell until it nearly touches the bottom. The cell is surrounded by a somewhat spacious cylinder made of platinum foil, which is employed as the anode. As the electrolyte, a very dilute solution of potassium sulphate is used.

The cell is filled with a 0.005 normal solution of the salt and then immersed in an ample supply of the same liquid, which is replenished from time to time to make good the water which passes through the porous wall and out of the horizontal tube above. The current pressure which we have found best suited to the removal of air is about 110 volts. The rate at which the water will pass through the cell wall varies greatly according to the texture. In very porous vessels the rate may exceed 1,000 cc. per hour, while in the case of the cells which were used for the present work, the endosmose amounted to only about 40 cc. per hour.

After 7 or 8 hours the salt solution is replaced by distilled water and the electrolysis is continued, with an occasional renewal of the water, until the conductivity of the liquid has been reduced to a minimum. The cell is then filled with and immersed in distilled water, which has been freed from air by boiling and it is not again disturbed until it is required for the deposition of the membrane.

The current pressure which is suitable for the deposition of a membrane depends on the character of the cell wall. The membrane which is formed on the inner wall of a highly porous vessel has always a low resistance and the higher the pressure of the current which is employed in its deposition, the lower is the resistance which can be secured. On the other hand, a membrane which is deposited in a cell of moderate, but uniform porosity may exhibit a resistance amounting to more than 100,000 ohms. This difference in cells, in respect to the resistance of the membranes which are deposited in them by the electrolytic process, appears to be due to the *endosmose* which, during the period of deposition, is always con-

siderable in a highly porous cell, and less in a cell of closer texture. Apparently the rupturing and detaching effects of the in-rushing water are greater in the former case than in the latter.

Very porous cells are wholly unfit for the measurement of osmotic pressure and they can, at best, be utilized for qualitative demonstrations only. The membranes which are produced in them are, judging by our experience with more than 100 such cells, easily ruptured and, without exception, permit the escape of the dissolved substance.

The arrangement which is made for the deposition of the membrane in a cell to be used for the measurement of pressure is as follows: A glass tube, with an internal diameter of about 5 mm. and with two narrow horizontal side tubes attached to it, is passed through a rubber stopper which fits the mouth of the cell. One of the side tubes—the upper one—is occupied by the platinum wire which is connected with the electrode, while the other—the lower one—serves for the overflow from the cell. The interior electrode (the cathode) is a narrow platinum cylinder about 40 mm. in length. To provide for the renewal of the solution within the cell, a short piece of rubber tubing is slipped over the upper end of the vertical glass tube and through this the stem of a small separating funnel is pushed down until its lower end is on a level with the bottom of the electrode.

The exterior electrode (the anode) is a cylinder of copper.

The solution of potassium ferrocyanide which is placed within the cell and that of the copper sulphate, which surrounds it, are both of 0.1 normal concentration. The former is renewed every 5 or 10 minutes by admitting, through the separating funnel, a volume of the fresh solution which is about equal to the capacity of the cell. The object of the frequent renewal of the solution of potassium ferrocyanide is to prevent an accumulation of alkali within the cell, the presence of which appears to have an injurious effect upon the membrane. In the case of some of the new electrolytically deposited cobalticyanide membranes, which are now under investigation in this laboratory, this difficulty is obviated by adding acetic acid to the liquid in the cell.

A current pressure of 110 volts is well adapted to the deposition of the membrane in any cell which is fit for quantitative measurements, and we have used approximately this voltage in all of our experiments. On several occasions we have raised the voltage to 250, but the consequences were wholly unsatisfactory. No good membranes were obtained by the higher pressure and, on breaking open the cells, a greenish-black deposit was found upon the wall in the proper place for the reddish-brown copper ferrocyanide. It was concluded that the membrane is decomposed at the higher voltage. No such effect has been observed where a pressure not exceeding 110 volts had been used.

When the circuit is first closed the resistance is found to be very high, owing to the absence of electrolytes from the cell wall, which, of course, in the beginning, is filled with fairly pure water. The current, in a short time, commences to increase and soon reaches a maximum which, in cells of good quality, will not exceed 100 milliamperes. From this point it declines continuously to a minimum, which is usually, though not always maintained for a considerable time, when the current again begins to rise, indicating a diminishing resistance of the membrane.

We have selected as the proper moment for breaking the circuit the time when the current, after having been for a period at a minimum, begins to increase. The following record of one of our cells, taken after the membrane had begun to form, will illustrate the usual course:

Time.	Voltage.	Current.
9.20 A. M.	109.8	0.0021
9.30 "	110.0	0.0016
9.50 "	110.0	0.0012
10.10 "	109.2	0.0012
10.20 "	109.9	0.0012
10.30 "	110.0	0.0012
10.40 "	110.0	0.0012
10.50 "	110.1	0.0012
11.00 "	110.1	0.0012
11.10 "	110.1	0.0012
11.20 "	110.1	0.0012
11.30 "	110.1	0.0013
11.40 "	110.0	0.0014

The minimum is not always so long maintained as in the case cited above. It may last less than a half hour.

The probable excellence of a cell can be quite accurately estimated by its conduct during the membrane-forming period. If the resistance rises rapidly to a high maximum, which is maintained for a long time before a decline sets in, the cell may confidently be expected to render satisfactory service in the measurement of pressure. If, on the other hand, the resistance of the membrane rises slowly to a maximum, which is not high and which is not long maintained, the cell will probably—though by no means certainly—fail to give entirely satisfactory results. We have come to regard, in a general way, 100,000 ohms or more as a proper resistance for a membrane, though good measurements have been obtained with cells in which the resistance of the membrane did not exceed 30,000 ohms.

One of two courses is followed when a membrane has failed to develop the high resistance which is regarded as a guarantee of its subsequent good behavior. The cell is soaked over night in distilled water and again subjected to the membrane-forming process on the following day; or it is set up with a rather concentrated solution of sugar to which a quantity of potassium ferrocyanide has been added and immersed in water containing an equivalent amount of copper sulphate. The concentration which is adopted for the membrane-forming salts in the latter case is 0.1 normal.

The membrane which is deposited, after soaking the cell in water, often exhibits a higher resistance than the first one and the improvement is sometimes so great as to justify the setting up of the cell for a measurement of pressure. The second course is, however, much more certain to lead to a satisfactory result, provided the faulty conduct of the membrane is not due to the imperfect character of the porous wall, in which case it is impossible by either procedure to produce a serviceable cell.

When a new cell is to be prepared for the measurement of pressure, we expel the air in the manner already described and then proceed to deposit the first membrane. If its conduct during the latter operation is encouraging, the cell is washed

with distilled water and set up with a half-normal, or even a normal solution of cane-sugar and allowed to develop pressure for several hours. The solution of sugar which is used in this first experiment with a cell is always made 0.1 N with potassium ferrocyanide and an equivalent amount of copper sulphate is added to the water on the outside. The purpose of adding the salts is two-fold. In the first place, if the structure of the porous wall is defective at any point, the location and also the character of the defect will be made apparent by the formation of colored spots or streaks upon the surface of the cell. In the second place, the membrane is usually strengthened by such treatment, apparently through a process of rupture in the weaker areas, which is followed by a mending of the rents.

In some cases, the pressure developed during the first trial of a cell rises rapidly and to a maximum which is known to be normal for the concentration of the solution. In others, the pressure develops more slowly and reaches the expected maximum very late or not at all. The former conduct is expected of a cell the membrane of which has a high resistance, and the latter of a cell with a membrane deficient in this respect.

Whatever the character of the result on the first trial may have been, the cell is taken down, washed and soaked for several hours in distilled water. It is then resubjected to the membrane-forming process, again washed and immediately thereafter it is filled and set up with a view to securing a measurement of osmotic pressure. However well the first membrane may have behaved, the second one usually surpasses it and it is not ordinarily necessary to repeat the treatment described above more than once before undertaking the measurement of pressure. These statements apply only to the cells which we have made in the laboratory. They do not hold good for the cells which have been made for us at the potteries. With the latter we have never succeeded in obtaining a measurement which we could regard as altogether satisfactory and it is in only a few of them out of many that we have been able to obtain anything more than very insignificant pressures. The reasons for this almost universal failure of the potters'

products to render the service required of them, we shall hope to make clear after we have finished the investigation referred to at the beginning of this paper.

7. The setting up of the cell in a satisfactory manner is a feat of some difficulty. The manipulation, when the stopper carrying the manometer is inserted in the cell, is necessarily of a strenuous character and calls for both strength and endurance on the part of the one who undertakes it. At this point the coöperation of two persons is essential.

The first step to be taken is to prepare the manometer. If this has been used in an earlier experiment, the enlargement at *j* and the tube for some distance beyond will be filled with a solution which must be removed and the space vacated must be filled with the solution, the pressure of which is to be measured.

The manometer is tilted to one side until the mercury runs back to the upper end of the enlargement *j*. The liquid remaining in the bulb is then removed by means of a twisted fragment of absorbent paper and the space is filled, through a very fine tube, with the solution the pressure of which is to be measured. Finally, the open end of the tube is immersed in some of the same solution and the manometer is restored to the vertical position. If the solution removed and that to be used differ considerably in concentration, the operation is several times repeated.

The implement which is employed to enable the surplus liquid to escape when the stopper is crowded into the cell is made from a common round file. A deep groove is cut on one side of the flat, untempered end, which is afterwards heated and bent to the form of a rather open hook. The curved end is filed down and smoothed off until it resembles, in the proportions of its parts, the poison fang of certain serpents. A tool of this form is easily inserted between the rubber stopper and the glass at *e*, Fig. I., and, if properly made, it does not lacerate the former nor scratch the latter. It is also used for the introduction of air when the cell is opened at the end of an experiment.

The cell is wrapped with absorbent material to prevent soil-

ing by the overflow from above and filled to the mouth with the solution. One of the operators holds the cell with one hand and manipulates the manometer with the other, the nut *h* resting, meanwhile, upon the back of the hand which holds the stopper. The duty of the other operator is to manipulate the "fang" until the stopper has been forced to a considerable depth into the glass tube and then to wrap the portion of the former which still remains outside of the latter. From the time when the stopper enters the tube until the nut *h* is brought down upon it and secured by the collar *g* there must not be the slightest relaxation of the pressure, otherwise air will enter the cell through the groove in the tool, or—after the removal of the tool—the mercury column will recede and allow some of the air in the manometer to escape around the bend into the bulb above.

A method of supporting the portion of the stopper remaining above the tube B, which we have found quite satisfactory, is to wrap it tightly with a strip of the sticky insulating tape which is used in electrical construction. It is for the purpose of making room for this that the diameter of the cavity in the bottom of the nut *h* is made a little greater than that of the stopper. The strip of tape is cut wide enough to cover the whole of the exposed portion of the stopper *k* and long enough to pass several times around it. After the removal of the tool, operator No. 2 seizes the stopper and holds it in place, while No. 1 removes his fingers to the top of the stopper to make room for the winding which is now attended to by No. 2. This finished, No. 2 again seizes the stopper and holds it until No. 1 has brought the nut *h* down to its place, when No. 2 turns the collar *g* until a rise of the mercury column indicates that the cell is safely closed.

Any failure to manipulate correctly while closing the cell is sure to be followed by serious trouble. The stopper must be driven quite deeply into the tube, otherwise it will be tipped to one side under high pressures and may, in consequence of such displacement, break the manometer or even permit the escape of some of the solution. Again, if the support given

to the stopper by the tape is insufficient it will "bulge" in the upper part and perhaps be driven out of the cell.

After closing the cell and placing it in the bottle *m*, the mercury in the manometer usually sinks for a time, remains stationary for a while and then begins to rise. This phenomenon is due to the fact that, while closing the cell, it is held in the hand and is warmed to a temperature above that of the water in the bottle. The shrinkage in the volume of the solution which follows the plunging of the cell into the colder water is not immediately compensated by the inflow of water through the membrane. After a time the two processes become equal and the mercury stands still for a few moments. Soon thereafter the flow of water into the solution exceeds the contraction of the latter and the mercury starts upward, in consequence of increasing pressure in the cell. When the mercury is seen to rise, the nut *h* is grasped with the wrench and the collar *g* is turned with the hand until a considerable additional pressure has been brought upon the solution. The purpose of this is to force the stopper somewhat further into the cell and to make the portion of it which is outside of the cell so rigid that no internal pressure can drive the lower end of the stopper upwards and out of its place. One who has had some experience in this manipulation can readily tell when the stopper is sufficiently rigid by the resistance which it offers when the collar is turned.

The pressure which is brought upon the contents of the cell, in the manner described, is never made equal to the osmotic pressure, owing to the danger of rupturing the membrane, though, in the case of concentrated solutions, it is sometimes carried to 14 or 15 atmospheres before it is felt to be safe to leave the stopper to itself.

8. In order to obtain correct determinations of osmotic pressure, the closest attention must be given to temperature conditions at several points. In the earlier stages of our work we were not so much impressed with the importance of this as we afterwards came to be and certain precautions, which should have been taken, were more or less neglected.

In the solutions upon which we have experimented, the relations of dissolved substance to solvent were *weight* relations exclusively, the unit weight of the water being, in all cases, 1000 grams, or that mass of the solvent the volume of which is 1 liter at the temperature of maximum density ; while the unit for the sugar was a gram-molecular weight (342.22 grams), or some decimal part thereof. The reason for selecting such proportions will appear later, when the significance of the results is discussed. The relations being those of weight only, it was a matter of no concern at what temperature the solutions were made, but the case is different when the cell is filled and closed. At that time the solution should have, as nearly as possible, the temperature at which the pressure is to be measured, since, if it has any other temperature the cell will contain, when closed, either too much or too little of the dissolved substance. The bearing of this fact upon one feature of the manipulation while setting up the cell is of some importance. The cell must then be tightly held in the hand for several minutes and the heating effect upon the solution within may be considerable unless measures are taken to protect the cell by wrapping it with non-conducting material. This precaution was neglected in our earlier experiments, but not in the later ones.

The thermal manifestations which have given us the most trouble are what we shall call *thermometer effects*. When a cell, in which the full pressure of the solution has been developed, is standing in a room where the temperature is fluctuating, the following movements of the mercury column in the manometer will be noticed : If the temperature of the room falls, the mercury column also falls, but always to a point *below* that which is normal for the concentration of the solution in the cell. If, after falling for a time, the temperature of the room becomes stationary, the mercury will rise again and if it remains constant for a sufficiently long time, the mercury will rise to the point which is normal for the concentration of the solution and there it will remain as long as the temperature conditions are unchanged. If, on the other hand, the temperature of the room rises, the mercury column also rises, but always to a point *too high* for the concentration of the solution. If, after rising

for a time, the temperature becomes stationary, the mercury again falls and always to the point which is normal for the solution, provided no new fluctuations of temperature set in.

The explanation of these phenomena is obvious. When the temperature is falling, the solution and the mercury enclosed in the cell contract *faster* than the water can get through the membrane for the purpose of maintaining the pressure which is normal to the solution and the mercury column, therefore, descends to an abnormally low point in the manometer. The solution, however, continues to take in water and, eventually, the proper degree of pressure is restored if the minimum temperature, after a fall, is sufficiently long maintained. On the other hand, when the temperature of the room rises, the enclosed solution and the mercury expand *faster* than the water is expelled from the cell and the consequence is that the mercury column in the manometer rises to a point which is abnormally high for the concentration of the solution, but the expulsion of water continues after the maximum temperature has been reached and the mercury begins to fall. If the maximum, after a rise of temperature, is sufficiently long maintained, the *over-pressure* will be reduced to the normal and the mercury will then become stationary.

This conduct on the part of the cell is very striking when the fluctuations of temperature are rapid and of considerable magnitude and it may lead to large errors in the determination of osmotic pressure. It is only when the changes of temperature are exceedingly slow that the passage of water in either direction, through the membrane, can keep pace with the contraction and expansion of the contents of the cell and the degree of exactness which can be secured in the measurement of osmotic pressure obviously depends, to a large extent, upon the weight which is attached to this fact.

In this connection we wish to speak of certain objections to a method of measuring osmotic pressure which has sometimes been practiced. The attempt has been made, on several occasions, to ascertain the pressure of solutions by bringing mechanical pressure to bear upon the contents of the cell until the mercury in the manometer rises to the highest point, becomes

stationary and then begins to fall. A minor objection to such procedure is the fact that it is not possible to ascertain whether the observed conduct of the mercury column, in the second and third stages, is due to a rupture of the membrane or to a *supposed* equilibrium between the mechanical and the osmotic pressures, which is afterwards disturbed by a slight excess of the former just at that point of time when the mercury begins to fall. The membrane is very liable to rupture under the strain of large and irregular accessions to the pressure upon it and it is not impossible that some of the measurements made by the method in question are, in reality, measurements of the strength of the membrane or of the support which is given to it by the porous wall behind.

A second and more serious objection to the method is the fact that pressures measured in this way are probably *overpressures* in all cases where the membrane is not broken, owing to the slowness with which any excess of water in the cell is expelled. The mercury column should come to a standstill when the increase of the mechanical pressure which is brought upon the solution is in equilibrium with the rate of expulsion of water from the cell, and it appears to the authors that this state is not likely to be reached until the mechanical pressure considerably exceeds the osmotic pressure. This would not be true, of course, if the solution could instantaneously discharge its excess of water when subjected to a mechanical pressure superior to its osmotic pressure. Since it cannot do so, but, on the contrary, requires a considerable time for the completion of the process, the *lowest* point to which the mercury *falls* after a rise, rather than the highest point which it reaches in the ascent, should be taken as the gauge of the osmotic pressure.

At first our cells were set up, without any external protection, in a room which was subject to the usual daily and nightly fluctuations of temperature, except that some measures were taken to moderate the extremes and to avoid very rapid changes of temperature. But the thermometer effects, of which we have spoken, were so pronounced that we began to protect the cells by placing them in boxes which were both lined and covered with flannel cloth and were opened only for

the purpose of determining the pressure. In this way the thermometer effects were considerably reduced, but not to a negligible magnitude. Later we adopted, and are still using, the arrangement which is shown in Figs. III., IV. and V. This consists of a box, Fig. III., having two doors, *a* and *c*, with an air space between them. The former, *a*, has a narrow plate-glass window, *b*, through which the height of the mercury in the manometer and also of the thermometers can be read without opening the inner door. The outer door, *c*, has, in its center, the smaller door, *d*, which is of the same size as the window, *b*. When a reading is to be made, it is necessary only to open the small door, *d*. The walls of the box are double and the space between is filled with inch-thick hair felt. Fig. IV., gives a sectional view of the box from front to back, in which the wooden walls and the hair between are designated by *a* and *b*, respectively. The small door, which is opened for the purpose of observing the manometer and thermometers, is indicated by *f* and the glass window by *i*. In the front part of the box there are two woolen curtains, *g*, which can be drawn aside or closed without opening the box. One of these is behind the inner door and the other between the two doors, *a* and *a*, shown in Fig. III. In the top of the box there are two holes, *e*, *e*, through which thermometers are lowered into the space below. There is also a small window, *d*, in the top, which was expected to serve for the illumination of the interior from above, but this has not been utilized for that purpose, owing to the effect of its use upon the temperature conditions within the box. The space below the window, *d*, is covered with the felt, *c*. Fig. V., gives the side-to-side sectional view of the box.

The arrangement, as described, was expected to render the changes of temperature so exceedingly slow as to eliminate the thermometer effects, but in this we were disappointed. They were smaller than before, but still not wholly negligible. Accordingly, the whole of the interior of the box, except in front of the glass window *b*, was lined with felt covered with flannel.

When the cell, after closing, is to be put in the box, a ther-

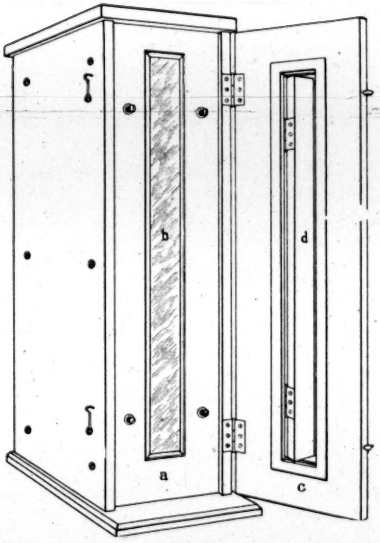

Fig. III.

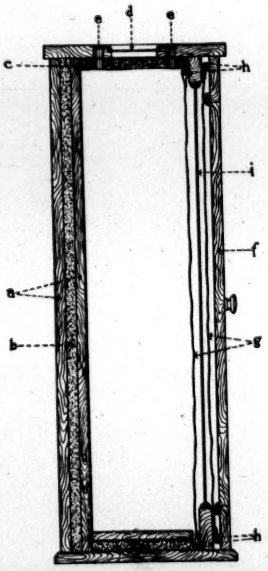

Fig. IV.

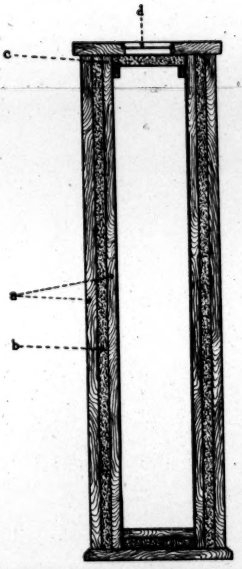

Fig. V.

mometer is strapped to the bottle *m*, Fig. I., with its bulb in contact with the glass. The cell, with the thermometer in place, is wrapped with a piece of felt, which is tied to the bottle. The protecting covering extends from the bottom of the bottle to the top of the nut *h*, Fig. I., but does not include any portion of the manometer. The space which is left between the upper, narrow portion of the cell and the felt is filled with hair.

After packing the cell in the manner described, it is placed on a felt base in the box and adjusted, with the aid of the telescope and plumb lines, until the manometer is vertical. By this time the osmotic pressure will have increased to such an extent that the further rise of the mercury in the manometer cannot sensibly affect its level in the bulb. Accordingly, certain readings are made for use in the later computations of pressure. They are the following: (1) The vertical distance between the level of the water in the bottle and that of the mercury in the manometer bulb; (2) the vertical distance between the height of the mercury in the bulb and the lines of reference on the manometer; (3) the vertical distance between the lines of reference on the manometer. Readings 1 and 2 are used in the subsequent computations of the pressure of the liquids in the manometer tube. If the distance between the top of the manometer and the upper line of reference has been ascertained previously, the only reading—except for temperature—which it is necessary to make when the pressure is to be determined is the distance between the upper line of reference and the top of the mercury column.

The whole interior of the box, from the bottom to a point half way up the manometer, or even higher, is carefully packed with hair, narrow strips of covered felt, somewhat longer than the internal width of the box, being used for the front retaining wall. The use of these strips, instead of one wide pad, for the front makes it possible to build up the packing by stages and, therefore, more carefully and conveniently than it could otherwise be accomplished. The thermometer which is used to register the temperature of the cell is a very long one, so that

the portion of the scale which is to be read through the window is in sight above the packing.

In Figs. IV., and V., only one thickness of felt is shown at the top of the box. There are, in reality, as many of these as are necessary to fill the space between the top of the manometer and the upper end of the box. Through holes in these, two long thermometers are pushed down until their bulbs are opposite the midway point of the column of air in the manometer. When the temperature is to be ascertained, the thermometers are drawn upwards until the mercury appears in sight above the top of the box.

All three of the thermometers which are used in the box are graduated to 0°.2.

When readings are to be made the curtains *g*, Fig. IV., are drawn aside and the small door *d*, Fig. III., is opened. If the light within is insufficient, that from an electric lamp without is thrown in from a distance during the final adjustment of the telescope.

9. Soon after beginning the measurement of the osmotic pressure of cane-sugar, under conditions which gave to the results a considerable degree of precision, it became apparent that the *mass of the solvent* plays a part which appears to have been unsuspected hitherto. We found—or *appeared* to discover—that a gram-molecular weight of the substance, dissolved in water and diluted to a liter volume, is not the normal standard for osmotic pressure. On the other hand, *when we dissolved a gram-molecular weight of cane-sugar (342.22 grams) in 1,000 grams of water, i. e., in that mass of the solvent which has the unit volume, 1 liter, at the temperature of maximum density—we found its osmotic pressure, at about 20°, in quite close accord with the pressure which a gram-molecular weight of hydrogen would exert, at the same temperature, if its volume were reduced to 1 liter, i. e., to that volume which the unit mass of the solvent has at the temperature of greatest density.*

The osmotic pressures of solutions ranging in concentration from 0.05 to 1 gram-molecular weight of sugar, in 1,000 grams of water, have since been measured and the results are all

reasonably in accord with the hypothesis of van 't Hoff, that *osmotic pressure obeys the laws of gases*, provided we accept, as the standard for the solvent, the fixed mass of 1,000 grams of water. These results, together with most of the data employed in calculating them, are presented in the latter part of this paper.

Our solutions, as stated above, were all made by dissolving a gram-molecular weight of cane-sugar, or some decimal part thereof, in 1,000 grams of water. The sugar used was "rock candy." The absolute purity of the material cannot be guaranteed, but several determinations of the carbon and hydrogen in it were made and the results were quite satisfactory. It was also tested for the products of inversion and found to be free from them.

The weights of the sugar and water were not corrected for displacement of air, hence they are slightly erroneous.

The solutions, made by dissolving a gram-molecular weight of sugar, or some decimal part of the same, in 1,000 grams of water, we shall call *weight-normal* to distinguish them from *volume-normal* solutions, *i. e.*, those which are made by dissolving the given weight of substance in water and diluting to a liter volume.

The specific gravities, at 20°, of the various concentrations of solution, the pressures of which were measured, were carefully determined with the use of Sprengel pycnometers and a constant bath. These are given in the table which follows, together with the equivalent *volume-normal* concentration of the solutions. There is also given, in the last column of the table, the true weight-normal concentrations of our solutions. The difference between the corresponding values in the first and last columns is the measure of the error resulting from a failure to correct the weights of sugar and water for air-displacement. The error is not large and may well be neglected in a first series of experiments. When the work is repeated, this and several other small errors pertaining to the present results will be excluded.

Table III.—Weight-Normal Solutions of Cane-Sugar.

Weight-normal concentration (uncorrected).	Specific gravity (in air) at 20° (uncorrected).	Grams of sugar in 1,000 grams of water (uncorrected).	Grams of sugar in 1 liter at 20° (uncorrected).	Equivalent volume-normal concentration (uncorrected).	Weight-normal concentration, corrected for air displacement.
0.05	1.006538	17.111	16.933	0.04948	0.04997
0.10	1.012920	34.222	33.518	0.09794	0.09995
0.20	1.025328	68.444	65.679	0.19192	0.19990
0.25	1.031240	85.555	81.271	0.23748	0.24988
0.30	1.037120	102.666	96.563	0.28216	0.29986
0.40	1.048460	136.888	126.280	0.36886	0.39981
0.50	1.059385	171.110	154.780	0.45228	0.49977
0.60	1.069858	205.332	182.240	0.53252	0.59972
0.70	1.079935	239.554	208.690	0.60981	0.69968
0.75	1.084805	256.665	221.550	0.64739	0.74966
0.80	1.089603	273.776	234.170	0.68428	0.79963
0 90	1.098920	307.998	258.750	0.75610	0.89959
1.00	1.107915	342.222	282.45	0.82534	0.99955

On taking down the cells after the measurement of pressure, the contents were immediately tested for inversion and evidence of the probable presence of invert sugar were found in all cases. In the more dilute solutions it did not amount to a quantity which could be determined and the evidence of its presence, even, was frequently of a dubious character. In the more concentrated solutions, on the other hand, the inversion which had taken place was of sufficient magnitude to permit of a quantitative estimation and, in such cases, the pressures observed have been corrected by deducting the theoretical osmotic pressure of one-half of the invert sugar which was found.

Whenever a cell was filled a portion of the solution was set aside in a closed vessel and, when the cell was opened at the close of the experiment, the contents were compared with the reserved portion with respect to the amount of inversion which had taken place in the interval, it was found, in every instance, that the inversion in the liquid taken from the cell was greater than in the other portion of the same solution. If the evidence of inversion in the dilute solutions was of a doubtful character in the one case, it was still more so, or altogether

lacking in the other, and the inversion in the reserved portions of the more concentrated solutions did not, in any instance, reach an amount which could be quantitatively estimated. It is, however, not safe to conclude that the greater *pressure* to which the contents of the cell were subjected was the sole cause of the greater inversion.

In all of our experiments we have added to the sugar solutions a small amount of potassium ferrocyanide and, to the water in which the cells were immersed, an equivalent amount of copper sulphate. The purpose of doing so has already been explained. The quantity of the former which was added to every solution of sugar was 0.0846 gram per 100 grams of water, while the copper sulphate added to the water outside of the cell amounted to 0.12488 gram per 100 grams of water. These quantities, if the salts are completely dissociated, are osmotically equivalent and their presence should not, therefore, affect the measurements of pressure. The greater inversion which was observed in the cell cannot, of course, be ascribed to the ferrocyanide, since the reserved portions of the solutions contained the same amount of it.

The method which was employed to determine the extent of the inversion was as follows: 0.5 cc., sometimes only 0.3 cc., of freshly prepared Fehling's solution was diluted with water and heated to the boiling-point. A measured portion of the sugar solution was then added and the liquid was boiled exactly 2 minutes. The experiment was repeated with fresh Fehling's solution and with smaller or larger quantities of the sugar solution, according as the color had, or had not wholly disappeared in the previous trial, until the exact volume of sugar solution required for decolorization had been ascertained.

We have not tested the accuracy of the method further than to satisfy ourselves that freshly prepared solutions of cane-sugar do not, under the same conditions, reduce Fehling's solution.

If a gram-molecular weight of a substance, dissolved in 1,000 grams of water, exerts an osmotic pressure equal to the pressure of a gas when a gram-molecular weight of it is reduced to a volume of 1 liter, and if osmotic pressure, like gas

pressure, obeys the law of Gay-Lussac, then the osmotic pressure of a weight-normal solution, at 0°, is 22.488 atmospheres and, at any higher temperature it is $22.488 + \frac{22.488}{273}$, or $22.488 + 0.0824t$ atmospheres.

Accordingly, if the osmotic pressure, P, which any solution is found to exert at the temperature t, is divided by $22.488 + 0.0824t$, the quotient is the concentration of the solution in terms of the weight-normal system, that is

$$\frac{P}{22.488 + 0.0824t} = \text{the weight-normal concentration of any solution.}$$

To find the molecular weight, M, of any substance from the osmotic pressure, P, which a known weight of it, W, exerts when dissolved in 1,000 grams of water, we have only to ascertain the value M in the proportion

$$\frac{P}{22.488 + 0.0824t} : 1 :: W : M.$$

The formula for the calculation of molecular weight from osmotic pressure is, therefore,

$$M = \frac{W(22.488 + 0.0824t)}{P}.$$

Our measurements have been tested by this formula and the results are given in the last column of each of the following tables.

The estimated pressure of 22.488 atmospheres for a gas, when the volume of a gram-molecular weight of it is reduced to 1 liter at 0°, is based on the value given by Morley for the weight of a liter of hydrogen, under standard conditions of temperature and pressure, at latitude 45°. This value is 0.089873 gram and, corrected to the latitude of this place, it becomes 0.089826 gram. Accepting 1.01 as the atomic weight of hydrogen, we have $\frac{2.02}{0.089826} = 22.488$. The value 22.443 is slightly more correct, but the difference between the two is

not sufficient to affect materially either the theoretical pressure given in column XI. of the tables or the molecular weights, calculated from osmotic pressure, which are recorded in column XIII.

It is hardly necessary to state that the deviations from the laws of Boyle and Gay-Lussac, which are observed in the conduct of air under pressure, have not been taken into account in our computations. Such refinements would, obviously, be inappropriate until after a better control has been obtained of the conditions under which the work is done, especially of temperature conditions.

The pressure of the atmosphere at the time the readings were made has been deducted before computing the values recorded in column X. of the tables.

0.05 Weight-Normal Solution—Experiment I.

Sugar dissolved in 1,000 grams of water = 17.111 grams.

Specific gravity of solution at 20° = 1.00653.

Grams of sugar in 1,000 cc. at 20° = 16.933.

Concentration of solution according to the *volume-normal* standard = 0.04948.

Cell used, A.

It had previously been employed to measure the pressure of a 0.10 weight-normal solution. When taken down it was soaked over night in distilled water and then subjected to the membrane-forming process.

Record.

March 27, 1905.

Time.	Voltage.	Current.	Resistance.
10.35 A. M.	109.3	0.0200	5465
10.40 "	109.3	0.0029	37690
10.50 "	109.3	0.0022	49690
11.00 "	109.3	0.0016	68330
11.40 "	109.3	0.0013	84077
12.15 P. M.	109.8	0.0012	91500
12.45 "	109.7	0.0011	99730
1.00 "	110.0	0.0010	110000
3.15 "	110.0	0.0011	100000

Manometer No. 3 was used.

Table IV.—Record of Observations.

(Experiment I. with 0.05 weight-normal solution.)

I. Time.	II. Top of the manometer.	III. Top of mercury column.	IV. Temperature of the solution.	V. Temperature of air in the manometer.	VI. Pressure of liquids in manometer.	VII. Pressure in atmospheres, uncorrected.	VIII. Calibration units of the air in manometer.	IX. Correction for inversion.	X. Pressure in atmospheres, corrected.	XI. Theoretical gas pressure.	XII. Difference between pressure found and calculated.	XIII. Molecular weight calculated from the equation $M = \frac{W(22.458 + 0.0824t)}{P}$.
March 27, 1905.					1.73	2.26	190.42	The inversion was very slight and could not be determined.	1.23	1.21	0.02	336.3
4.30 P. M.	441.6	666.4			2.04	2.27	190.42		1.23	1.21	0.02	336.1
8.30 "	441.8	668.5										
March 28.												
8.45 A. M.	441.6	645.7	20°.5	19°.35	0.35 Atmosphere.	2.30	185.49	Atmospheric pressure not deducted.	1.28	1.21	0.07	323.3
12.00 M.	441.6	644.45	20°.36	20°.04		2.34	182.65		1.31	1.21	0.10	316.1
4.15 P. M.	441.65	639.6	20°.6	21°.55		2.37	179.89		1.34	1.21	0.13	309.4
6.00 "	441.55	637.25	20°.8	22°.26								
9.15 "	441.65	634.80	21°.2	22°.32								
March 29.												
8.30 A. M.	441.7	639.4	21°.16	20°.4		2.32	185.49		1.28	1.21	0.07	323.9
12.00 M.	441.66	640.65	20°.98	20°.61		2.31	187.43		1.26	1.21	0.05	327.5
3.00 P. M.	441.60	639.82	21°.1	21°.45		2.32	185.49		1.28	1.21	0.07	323.8
5.30 "	441.63	637.9	21°.24	22°.05		2.34	183.53		1.30	1.22	0.08	319.7
												324.0

Number of calibration units of air, under standard conditions, in the manometer = 357.99.

The cell was set up at 3.45 P. M., March 27, with a 0.05 weight-normal solution which contained 0.0846 gram of $K_4Fe(CN)_6.3H_2O$ per 100 grams of H_2O. The water on the outside contained 0.12488 gram $CuSO_4.5H_2O$ per 100 grams of water. The initial pressure was 1.6 atmospheres.

Values Used in Computations.

0.003665, for temperature coefficient of gases.

0.089826, for weight of a liter of H_2 at Baltimore.

22.488, atmospheres pressure for a gram-molecular weight of H_2 reduced, at 0°, to 1 liter volume.

Comments.

The minimum and maximum difference between pressures found and calculated are 0.02 atmosphere and 0.13 atmosphere, respectively (column XII.). These, though seemingly not very far apart, correspond to a large difference in molecular weights, *i. e.*, 26.9 (column XIII.).

It is to be noted that, when molecular weights are determined by osmotic pressure, the accuracy of the results increases with the concentration of the solutions; in other words, a given error of measurement diminishes in importance as the value of W in the formula $M = \frac{W(22.488 + 0.0824t)}{P}$ increases.

0.05 Weight-Normal Solution—Experiment II.

Sugar dissolved in 1,000 grams of water = 17.111 grams.

Specific gravity of solution at 20° = 1.00653.

Grams of sugar in 1,000 cc. at 20° = 16.933.

Concentration of the solution according to the *volume-normal* standard = 0.04948.

Cell used, A.

It was soaked in water over night after Experiment I. with a 0.05 weight-normal solution and then subjected to the membrane-forming process.

Record.

March 30, 1905.

Time.	Voltage.	Current.	Resistance.
9.20 A. M.	109.8	0.0021	52280
9.30 "	110.0	0.0016	68730
9.50 "	110.0	0.0012	91670
10.10 "	109.2	0.0012	91000
10.20 "	109.9	0.0012	91590
10.30 "	110.0	0.0012	92670
10.40 "	110.0	0.0012	91670
10.50 "	110.1	0.0012	91750
11.00 "	110.1	0.0012	91750
11.10 "	110.1	0.0012	91750
11.20 "	110.1	0.0012	91750

Manometer No. 3 was used.

Number of calibration units of air = 357.99.

The cell was set up at 12.00 M., March 30, with a 0.05 weight-normal solution, the solution containing the same proportion of $K_4Fe(CN)_6.3H_2O$ as in Experiment I. and the water without the same proportion of $CuSO_4.5H_2O$ as in Experiment I. The initial pressure, uncorrected, was 1.8 atmospheres.

Values Used in Computations.

0.003665, for temperature coefficient of gases.

0.089826, for weight of a liter of H_2 at Baltimore.

22.488 atmospheres pressure for a gram-molecular weight of H_2 reduced, at 0°, to a volume of 1 liter.

Comments.

The average of the molecular weights calculated from the osmotic pressures observed in Experiment I., with a 0.05 weight-normal solution, is 324.0, while the corresponding value in the case of Experiment II. is 331.7. These numbers are decidedly low for the molecular weight of cane-sugar (18.22 and 10.52 units, respectively), but it is to be observed that these were among the first experiments which were made and that, at the time of making them, we had not begun to employ the precautions which were afterwards taken to avoid rapid changes of temperature.

Table V.—Record of Observations.

(Experiment II. with 0.05 Weight-Normal Solution.)

I. Time.	II. Top of the manometer.	III. Top of mercury column.	IV. Temperature of the solution.	V. Temperature of air in the manometer.	VI. Pressure of liquids in the manometer.	VII. Pressure in atmospheres, uncorrected.	VIII. Calibration units of the air in manometer.	IX. Correction for inversion.	X. Pressure in atmospheres, corrected.	XI. Theoretical gas pressure.	XII. Difference between pressure found and calculated.	XIII. Molecular weight calculated from the equation $M = \frac{W(22.488 + 0.0824t)}{P}$.
March 30, 1905.												
2.30 P. M.	436.70	677.4										
5.30 "	436.25	665.14	21°.2	21°.87	0.35	1.91	197.78	Inversion insufficient for quantitative measurement.	1.16	1.21	—0.05	357.1
8.30 "	436.20	665.10	21°.1	21°.87	Atmosphere.	1.99	186.45		1.27	1.21	0.06	326.1
March 31.												
8.30 A. M.	436.23	645.23	20°.9	19°.5		2.11	193.51		1.20	1.21	—0.01	345.1
12.00 M.	436.52	642.77	20°.8	20°.43		2.21	184.53		1.29	1.21	0.08	320.3
5.30 P. M.	436.63	637.17	20°.9	21°.55		2.23	187.43		1.26	1.21	0.05	328.7
8.30 "	436.15	633.70	20°.2	22°.00		2.30	184.53		1.29	1.21	0.08	320.3
April 1.						Atmospheric pressure not deducted.						
8.30 A. M.	436.45	634.76	20°.8	19°.99		2.32	186.45		1.27	1.21	0.06	326.1
2.45 P. M.	436.63	634.28	20°.73	20°.82		2.32	184.53		1.29	1.21	0.08	320.9
4.50 "	436.35	634.00	20°.8	20°.90		2.32	185.49		1.28	1.21	0.07	323.5
												331.7

It is to be noted, further, that in very dilute solutions a small absolute error in the measurement of pressure corresponds to a large error in the estimated molecular weight. For example, a mistake of 0.1 atmosphere in the measurement of the pressure of a 0.05 weight-normal solution of cane-sugar gives an error of 30.4 units in the molecular weight.

0.10 Weight-Normal Solution—Experiment I.

Sugar dissolved in 1,000 grams of water = 34.222 grams.
Specific gravity of solution at 20° = 1.01293.
Grams of sugar in 1,000 cc. at 20° = 33.518.

Concentration of the solution according to the *volume-normal* standard = 0.09794.

Cell A. It had been used with a 0.25 weight-normal solution. It was taken down March 20, 1905, soaked over night of March 20 and subjected to the membrane-forming process March 21.

Record.

March 21, 1905. Started at 2.55 P. M.

Time.	Voltage.	Current.	Resistance.
3.00 P. M.	107.2	0.0023	46610
3.15 "	107.0	0.0016	66870
3.22 "	107.0	0.0013	82310
3.45 "	107.3	0.0013	82540
4.00 "	107.3	0.0013	82540
4.15 "	107.3	0.0012	89420
4.30 "	107.0	0.0012	89165

Manometer No. 3 was used.

Number of calibration units of air in the manometer = 357.99.

The cell was set up at 4.50 P. M., March 21, with a 0.10 weight-normal solution.

The solution within contained the usual proportion of $K_4Fe(CN)_6.3H_2O$, *i. e.*, 0.0846 gram per 100 grams of H_2O, and the water without the usual amount of $CuSO_4.5H_2O$, *i. e.*, 0.12488 gram per 100 grams of H_2O. Initial pressure = 1.2 atmospheres.

Values Used in the Computations.

0.003665, for temperature coefficient of gases.

0.089826, for weight of a liter of H_2 at Baltimore.

22.488, atmospheres pressure for a gram-molecular weight of H_2 reduced, at 0°, to a volume of 1 liter.

Comments.

This experiment illustrates well the effect of fluctuating temperature upon the measurement of osmotic pressure. The night of March 23 was cold and the temperature of the room fell to a low point. The consequence is apparent from the readings which were made the following morning.

At this time the only precaution which was taken to protect the cell consisted in placing it in a wooden box which was lined and covered with woolen cloth. This provision was found wholly inadequate whenever the temperature at night differed considerably from that of the preceding and following days.

A mistake of 0.1 of an atmosphere, in the measurement of the osmotic pressure of a 0.1 weight-normal solution, produces an error of 15.2 units in the estimated molecular weight of cane-sugar.

0.10 Weight-Normal Solution—Experiment II.

Sugar dissolved in 1,000 grams of water = 34.222 grams.

Specific gravity of solution at 20° = 1.01293.

Grams of sugar in 1,000 cc. at 20° = 33.518.

Concentration of the solution according to the *volume-normal* standard equal 0.09794.

Cell A was used. It was soaked in distilled water from 8.30 A. M. to 3.00 P. M., after use in Experiment I., with a 0.10 weight-normal solution and then subjected to the membrane-forming process.

Table VI.—Record of Observations.

(Experiment I. with 0.10 Weight-Normal solution.)

I. Time.	II. Top of the manometer.	III. Top of mercury column.	IV. Temperature of the solution.	V. Temperature of air in the manometer.	VI. Pressure of liquids in the manometer.	VII. Pressure in atmospheres, uncorrected.	VIII. Calibration units of the air in the manometer.	IX. Correction for inversion.	X. Pressure in atmospheres, corrected.	XI. Theoretical gas pressure.	XII. Difference between pressure found and calculated.	XIII. Molecular weight calculated from the equation $M = \frac{W(22.488 + 0.0324t)}{p}$.
March 21, 1905.					0.45 Atmosphere.							
5.50 P. M.	402.73	682.3				1.54						
March 22.												
9.00 A. M.	402.70	552.7	16°.0	15°.87		2.99						
12.00 M.	402.50	538.6	17°.7	18°.96		3.30	116.65		2.52	2.41	0.11	327.7
4.00 P. M.	402.55	527.56	19°.9	21°.26		3.56			2.50	2.41	0.09	330.5
5.30 "	402.40	528.00	20°.1	20°.98		3.54	117.31					
March 23.												
9.00 A. M.	402.54	544.48	15°.62	14°.25		3.17	135.65		2.07	2.37	[−0.30!]	[393.0!]
12.00 M.	402.70	536.40	16°.5	16°.9		3.35	126.59		2.27	2.38	−0.11	359.5
2.45 P. M.	402.50	527.80	18°.9	19°.1		3.57	117.6		2.49	2.40	0.09	330.4
												337.0

Atmospheric pressure not deducted

The inversion was insufficient to permit of a quantitative determination.

Table VIII.—Record of Observations.

(Experiment II. with 0.10 Weight-Normal Solution.)

I. Time.	II. Top of manometer.	III. Top of mercury column.	IV. Temperature of the solution.	V. Temperature of air in the manometer.	VI. Pressure of liquids in the manometer.	VII. Pressure in atmospheres, uncorrected.	VIII. Calibration units of the air in the manometer.	IX. Correction for inversion.	X. Pressure in atmospheres, corrected.	XI. Theoretical gas pressure.	XII. Difference between pressure found and calculated.	XIII. Molecular weight calculated from the equation $M = \frac{W(22.488 + 0.0342t)}{P}$.
March 24, 1905.						Atmospheric pressure not deduct'd						
5.40 P. M.	440.9	660.1				2.11						
8.30 "	440.9	614.6	20°.15	20°.2		2.63						
March 25.					0.45 Atmosphere.							
8.30 A. M.	441.1	574.0	18°.5	16°.78		3.37	122.92	The inversion was insufficient to permit of quantitative determination.	2.36	2.40	—0.04	348.0
12.00 M.	441.0	571.48	18°.54	18°.42		3.46	119.71		2.44	2.40	0.04	336.9
3.00 P. M.	440.9	568.5	18°.64	19°.46		3.49	118.74		2.46	2.40	0.06	334.5
5.00 "	440.1	566.75	18°.9	19°.85		3.52	117.19		2.50	2.40	0.10	329.4
8.45 "	440.9	565.9	19°.18	19°.86		3.50						
March 26.												
10.30 A. M.	441.0	568.2	18°.5	18°.92		3.51	118.70		2.46	2.40	0.06	334.0
12.30 P. M.	441.1	568.19	18°.5	18°.45		3.51	119.74		2.44	2.40	0.04	336.8
												336.6

Record.

March 24, 1905.

Time.	Voltage.	Current.	Resistance.
3.00 P. M.	108.0	0.0100	10800
3.15 "	108.0	0.0022	49090
3.25 "	108.0	0.0016	67500
3.40 "	108.0	0.0013	83085
4.00 "	108.0	0.0013	83085
4.10 "	108.0	0.0012	90000
4.20 "	107.5	0.0012	89585

The manometer was No. 3.

Number of calibration units of air = 357.99.

The cell was set up at 5.30 P. M., March 24, 1905, with a 0.10 weight-normal sugar solution containing the usual amount of $K_4Fe(CN)_6.3H_2O$.

The initial pressure, uncorrected, was 2.11 atmospheres.

Values Used in Computations.

0.003665, for temperature coefficient of gases.

0.089826, for weight of 1 liter of H_2 at Baltimore.

22.488, atmospheres pressure for a gram-molecular weight of H_2 reduced, at 0°, to a volume of 1 liter.

0.20 Weight-Normal Solution—Experiment I.

Sugar dissolved in 1,000 grams of water = 68.444 grams.

Specific gravity of solution at 20° = 1.02530.

Grams of sugar in 1,000 cc. at 20° = 65.679.

Concentration of the solution according to the *volume-normal* standard = 0.19192.

Cell B was used for the first time in this experiment for the measurement of pressure. It had been set up the previous day with a 0.20 weight-normal solution and allowed to develop pressure. The following record was made. Set up at 5.15 P. M., April 10 :

Record.

April 10, 1905.	Pressure uncorrected.	Temperature.
8.30 P. M.	4.95	20°.40
April 11.		
9.00 A. M.	4.84	19°.5
12.00 M.	4.89	19°.5
3.00 P. M.	4.98	19°.8
5.00 "	5.04	20°.2

The cell was taken down, soaked over night in distilled water and again subjected to the membrane-forming process on April 12.

Record.

April 12, 1905.

Time.	Voltage.	Current.	Resistance.
9.45 A. M.	110.6	0.0025	44240
9.50 "	110.6	0.0021	52670
10.00 "	110.7	0.0017	65120
10.05 "	110.8	0.0014	79140
10.15 "	110.7	0.0013	85155
10.25 "	110.7	0.0013	85155
10.35 "	110.7	0.0013	85155
10.45 "	110.7	0.0012	92250
10.55 "	110.7	0.0012	92250
11.05 "	110.7	0.0013	85155
11.15 "	110.7	0.0014	79140

The cell was set up at 11.40 A. M., April 12, with a 0.20 weight-normal solution containing the usual quantity of potassium ferrocyanide. Initial pressure = 4.01 atmospheres.

Manometer No. 3 was used after fourth filling.

Number of calibration units of air = 399.05.

Values Used in the Computations.

0.003665, for temperature coefficient of gases.

0.089826, for weight of 1 liter of H_2 at Baltimore.

22.488 atmospheres of pressure for a gram.molecular weight of H_2 when reduced, at 0°, to a volume of 1 liter.

Comments.

Only two cells were used in this work. They are designated by the letters A and B. The latter was used for the first time in this experiment. Attention is called to the rapidity with which the pressure approached a maximum. The cell was set up at 11.40 A. M. and at 3.00 P. M. the pressure had reached 4.75 atmospheres (corrected), the theoretical pressure at the same temperature being 4.85 atmospheres.

A mistake of 0.1 atmosphere in the measurement of the osmotic pressure of a 0.2 weight-normal solution produces an error of 7.6 units in the estimated molecular weight of cane-sugar.

Table VIII.—Record of Observations.

(Experiment I. with 0.20 Weight-Normal Solution.)

I. Time.	II. Top of the manometer.	III. Top of mercury column.	IV. Temperature of the solution.	V. Temperature of air in the manometer.	VI. Pressure of liquids in the manometer.	VII. Pressure in atmosphere, uncorrected.	VIII. Calibration units of the air in the manometer.	IX. Correction for inversion.	X. Pressure in atmosphere, corrected.	XI. Theoretical gas pressure.	XII. Difference between pressure found and calculated.	XIII. Molecular weight calculated from the equation $M = \frac{W(22.488 + 0.0824t)}{p}$.
April 12, 1905.												
3.30 P. M.	457.12	538.53	21°.75	21°.30	0.497 Atmosphere.	5.82	75.93	Insufficient for quantitative determination.	4.75	4.85	—0.10	349.8
5.00 "	457.00	538.33	21°.70	21°.37		5.84	75.90		4.75	4.85	—0.10	349.8
8.30 "	457.35	538.00	21°.53	21°.25		5.89	75.23		4.80	4.85	—0.05	345.6
April 13.						Atmospheric pressure not deducted.						
8.30 A. M.	457.35	537.91	20°.10	18°.87		5.89	75.75		4.77	4.83	—0.06	346.4
12.30 P. M.	457.35	538.00	19°.64	18°.70		5.92	75.89		4.75	4.82	—0.07	347.3
3.00 "	447.15	537.85	19°.68	19°.30		5.89	75.71		4.77	4.82	—0.05	345.9
5.00 "	457.06	537.62	19°.70	19°.70		5.90	75.54		4.78	4.82	—0.04	345.2
												347.1

0.20 Weight Normal Solution—Experiment II.

Sugar dissolved in 1,000 grams of water = 68.444 grams.

Specific gravity of solution at 20° = 1.0253.

Grams of sugar in 1,000 cc. at 20° = 65.679.

Concentration of the solution according to the *volume-normal* standard = 0.019192.

Cell A was used. It had been previously set up with a 0.90 weight-normal solution, but after a pressure of 14.9 atmospheres had been developed the stopper was dislodged. The cell was then taken down, soaked in distilled water over night and again subjected to the membrane-forming process.

Record.

April 25, 1905.

Time.	Voltage.	Current.	Resistance.
3.21 P. M.	110	0.0030	56667
3.25 "	110	0.0018	61110
3.30 "	110	0.0015	73333
3.40 "	110	0.0013	84615
3.50 "	110	0.0012	91668
4.00 "	110	0.0011	100000
4.10 "	110	0.0011	100000
4.20 "	110	0.0011	100000
4.30 "	110	0.0011	100000
4.40 "	110	0.0011	100000
4.50 "	110	0.0011	100000
5.00 "	110	0.0011	100000

Manometer No. 3 was used after the fifth filling.

Number of calibration units of air = 401.94.

Values Used in the Computations.

0.003665, for temperature coefficient of gases.

0.089826, for weight of a liter of H_2 at Baltimore.

22.488, atmospheres pressure for a gram-molecular weight of H_2 reduced, at 0°, to a volume of 1 liter.

The cell was set up at 5.30 P. M., April 25.

The initial pressure, uncorrected, was 5.38 atmospheres.

Table IX.—Record of Observations.

(Experiment II. with 0.20 Weight-Normal Solution.)

I. Time.	II. Top of the manometer.	III. Top of mercury column.	IV. Temperature of the solution.	V. Temperature of air in the manometer.	VI. Pressure of liquids in the manometer.	VII. Pressure in atmospheres, uncorrected.	VIII. Calibration units of air in the manometer.	IX. Correction for inversion.	X. Pressure in atmospheres, corrected.	XI. Theoretical gas pressure.	XII. Difference between pressures found and calculated.	XIII. Molecular weight calculated from the equation $M = \frac{W(22.488 + 0.0834t)}{P}$.
April 25, 1905.												
8.45 P. M.	458.34	544.38	22°.2	21°.7	0.50 Atmosphere.	5.50	75.93	Insufficient for quantitative determination.	4.79	4.84	—0.05	346.1
April 26.						Atmospheric pressure not deducted.						
9.00 A. M.	458.48	539.59	21°.22	20°.22		5.81	75.93		4.79	4.84	—0.05	345.9
12.00 M.	458.31	539.45	20°.9	20°.2		5.81	75.53		4.82	4.84	—0.02	342.6
3.00 P. M.	458.13	538.91	20°.8	20°.5		5.83	74.99		4.86	4.84	0.02	340.8
5.00 "	458.36	538.62	20°.82	20°.82		5.87	74.99		4.89	4.84	0.05	338.9
8.30 "	458.46	538.35	20°.9	21°.0		5.90	74.50					
April 27.												
9.00 A. M.	458.33	538.45	20°.8	20°.5		5.88	75.12		4.85	4.84	0.01	341.5
												342.6

0.25 Weight-Normal Solution—Experiment I.

Sugar dissolved in 1,000 grams of water = 85.55 grams.

Specific gravity of the solution at 20° = 1.03120.

Grams of sugar in 1,000 cc. at 20° = 81.271.

Concentration of the solution according to the *volume-normal* standard = 0.23748.

Cell A was used. It had been previously set up with a 0.5 weight-normal solution. It was soaked one-half day in distilled water, then subjected to the membrane-forming process, March 16.

Record.

March 16, 1905.

Time.	Voltage.	Current.	Resistance.
3.00 P. M.	114.0	0.0024	47500
3.15 "	113.2	0.0014	80860
3.25 "	112.5	0.0012	93750
3.50 "	112.5	0.0011	102270
4.20 "	112.0	0.0010	112000
4.45 "	111.5	0.0010	111500

Manometer No. 3 was used after the second filling.

Number of calibration units of air—reduced to standard conditions = 380.08.

The cell was set up at 5.00 P. M., March 16, 1905. The solution contained 0.0846 gram $K_4Fe(CN)_6.3H_2O$ per 100 grams of H_2O and the water without contained 0.12488 gram $CuSO_4.5H_2O$ per 100 grams of H_2O.

Values Used in the Computations.

0.003665, for temperature coefficient of gases.

0.089826, for weight of 1 liter of H_2 at Baltimore.

22.488, atmospheres pressure for a gram-molecular weight of H_2 when reduced, at 0°, to a volume of 1 liter.

The initial pressure, uncorrected, was 3.7 atmospheres.

A mistake of 0.1 atmosphere, in the measurement of the osmotic pressure of a 0.25 weight-normal solution, produces an error of 5.67 units in the estimated molecular weight of cane-sugar.

Table X.—Record of Observations.

(Experiment I. with 0.25 Weight-Normal Solution.)

I. Time.	II. Top of the manometer.	III. Top of mercury column.	IV. Temperature of the solution.	V. Temperature of air in the manometer.	VI. Pressure of liquids in the manometer.	VII. Pressure in atmospheres, uncorrected.	VIII. Calibration units of air in the manometer.	IX. Correction for inversion.	X. Pressure in atmospheres, corrected.	XI. Theoretical gas pressure.	XII. Difference between pressure found and calculated.	XIII. Molecular weight calculated from the equation $M = \frac{W(22.488 + 0.0524t)}{p}$
March 16, 1905.												
5.30 P. M.	402.9	517.8				3.92		Insufficient for quantitative determination.				
5.45 "	402.9	504.1				4.13						
8.30 "	402.65	472.65	23°.2	23°.75		6.24						
March 17.						Atmospheric pressure not deducted.						
8.45 A. M.	402.7	465.6	22°.4	22°.45	0.53 Atmosphere.	6.91	58.37		6.04	6.08	—0.04	344.7
12.00 M.	402.5	464.6	23°.0	23°.53		6.99	57.41		6.15	6.09	0.06	339.2
2.45 P. M.	402.3	464.1	23°.75	24°.35		7.02	56.80		6.22	6.11	0.11	336.2
5.00 "	402.4	464.7	23°.90	24°.26		6.97	57.46		6.14	6.11	0.03	340.9
8.15 "	402.2	464.7	24°.2	24°.33		6.95	57.64		6.12	6.12	0.00	342.2
												340.6

0.25 Weight-Normal Solution—Experiment II.

Sugar dissolved in 1,000 grams of water = 85.555 grams.

Specific gravity of solution at 20° = 1.03124.

Grams of sugar in 1,000 cc. at 20° = 81.271.

Concentration of the solution according to the *volume-normal* standard = 0.23748.

After experiment No. 1 with a 0.25 weight-normal solution, cell A was soaked in distilled water till 2.55 P. M., March 18. It was then subjected to the membrane-forming process.

Record.

March 18, 1905.

Time.	Voltage.	Current.	Resistance.
3.05 P. M.	110.0	0.0022	50000
3.25 "	110.0	0.0016	68750
3.45 "	110.1	0.0165	6673
4.00 "	110.3	0.0017	64880
4.15 "	110.3	0.0017	64880

The cell was set up at 5.20 P. M., March 18, with a 0.25 weight-normal solution containing the usual amount of potassium ferrocyanide.

The initial pressure, uncorrected, was 2.9 atmospheres.

Manometer No. 3 was used.

Number of calibration units of air, reduced to standard conditions = 380.08.

Values Used in the Computations.

0.003665, for temperature coefficient of gases.

0.089826, for weight of 1 liter of H_2 at Baltimore.

22.488, atmospheres pressure for a gram-molecular weight of H_2 when reduced, at 0°, to a volume of 1 liter.

0.30 Weight-Normal Solution—Experiment I.

Sugar dissolved in 1,000 grams of water = 102.666 grams.

Specific gravity of solution at 20° = 1.03712.

Grams of sugar in 1,000 cc. at 20° = 96.563.

Concentration of the solution according to the *volume-normal* standard = 0.28213.

Cell A was used. It had previously been used in Experi-

Table XI.—Record of Observations.

(Experiment II. with 0.25 Weight-Normal Solution.)

I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.	XI.	XII.	XIII.
Time.	Top of manometer.	Top of mercury column.	Temperature of the solution.	Temperature of air in the manometer.	Pressure of liquids in the manometer.	Pressure in atmospheres, uncorrected.	Calibration units of air in the manometer.	Correction for inversion.	Pressure in atmospheres, corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.	Molecular weight calculated from the equation $M = \frac{W(22.458 + 0.0342t)}{P}$
March 18, 1905.												
5.45 P. M.	400.1	542.7				3.18						
8.45 "	398.9	474.7	24°.0	23°.97		5.79						
March 19.						Atmospheric pressure not deducted.						
9.45 A. M.	398.5	463.3	21°.9	21°.60	0.53	6.75						
12.00 M.	398.8	463.3	21°.75	21°.45		6.71						
1.00 P. M.	398.75	462.14	21°.75	21°.55		6.86	59.00		5.97	6.08	—0.11	348.5
4.00 "	398.78	462.32	21°.90	21°.95		6.84	59.05		5.96	6.07	—0.11	348.7
March 20.					Atmosphere.							
8.30 A. M.	398.77	462.60	20°.9	20°.65		6.81	59.59		5.92	6.05	—0.13	349.9
12.15 P. M.	398.86	461.45	21°.35	21°.41		6.94	58.28		6.05	6.06	—0.01	342.9
5.20 "	398.60	461.62	21°.4	21°.25		6.89	58.71		6.00	6.06	—0.06	345.8
												347.2

ment II. with a 0.05 weight-normal solution. At the close of this experiment the cell was soaked over night in distilled water and then subjected to the membrane-forming process.

Record.

April 3, 1905.

Time.	Voltage.	Current.	Resistance.
10.30 A. M.	110.0	0.0100	11000
10.40 "	110.0	0.0013	84615
11.00 "	110.0	0.0010	110000
11.20 "	110.0	0.0010	110000
11.25 "	110.2	0.0010	110200
11.40 "	110.2	0.0010	110200

The cell was not set up immediately, but was soaked over night in distilled water and again subjected to the membrane-forming process on the following day.

Record.

April 4, 1905.

Time.	Voltage.	Current.	Resistance.
9.20 A. M.	111.2	0.0012	92670
9.30 "	111.5	0.0011	101360
9.50 "	111.6	0.0009	124000
10.00 "	111.6	0.0009	124000
10.10 "	107.0	0.0009	118900
10.20 "	106.5	0.0009	118330
10.30 "	106.5	0.0009	118330
10.40 "	111.0	0.0009	123330
10.50 "	111.0	0.0009	123330

Manometer No. 4 was used.

Number of calibration units reduced to standard conditions = 402.66.

Values Used in the Computations.

0.003665, for temperature coefficient of gases.

0.089826, for weight of 1 liter of H_2 at Baltimore.

22.488, atmospheres pressure for a gram-molecular weight of H_2 when reduced, at 0°, to a volume of 1 liter.

The cell was set up at 11.15 A. M., April 4.

The initial pressure, uncorrected, was 3.15 atmospheres.

Table XII.—Record of Observations.

(Experiment I. with 0.30 Weight-Normal Solution.)

I. Time.	II. Top of the manometer.	III. Top of mercury column.	IV. Temperature of the solution.	V. Temperature of air in the manometer.	VI. Pressure of liquids in the manometer.	VII. Pressure in atmospheres, uncorrected.	VIII. Calibration units of air in manometer.	IX. Correction for inversion.	X. Pressure in atmospheres, corrected.	XI. Theoretical gas pressure.	XII. Difference between pressure found and calculated.	XIII. Molecular weight calculated from the equation $M = \frac{W(22.486 - 0.824f)}{f}$
April 4, 1905.												
12.10 P. M.	470.90	599.70				3.75						
3.15 "	468.50	535.10	19°.90	20°.05		6.93						
5.15 "	468.50	528.00	19°.90	20°.15		7.54						
8.30 "	468.10	523.45	19°.92	20°.14		8.25						
April 5.												
9.00 A. M.	468.10	521.60	19°.43	18°.62	0.47 Atmosphere.	8.54	52.10		7.19	7.22	—0.03	343.9
12.00 M.	468.00	521.40	19°.40	19°.46		8.56	51.87		7.23	7.22	0.01	342.0
3.00 P. M.	468.23	520.80	19°.70	20°.65		8.63	50.87		7.38	7.23	0.15	335.4
5.30 "	468.15	520.60	19°.94	20°.60		8.68	50.76		7.20	7.24	—0.04	344.1
April 6.												
8.45 A. M.	468.17	521.45	18°.70	17°.22		8.56	52.16		7.19	7.21	—0.02	343.1
12.00 M.	468.00	521.47	18°.50	17°.9		8.53	52.21		7.18	7.21	—0.03	343.6
												342.0

Atmospheric pressure not deducted.

Insignificant for quantitative determination.

A mistake of 0.1 atmosphere in the measurement of the osmotic pressure of a 0.3 weight-normal solution produces an error of 5.4 units in the estimated molecular weight of cane-sugar.

0.30 Weight-Normal Solution—Experiment II.

Sugar dissolved in 1,000 grams of water = 102.666 grams.

Specific gravity of solution at 20° = 1.03712.

Grams of sugar in 1,000 cc. at 20° = 95.563.

Concentration of the solution according to the *volume-normal* standard = 0.28216.

Cell A was used. After Experiment I., with a 0.30 weight-normal solution, it was soaked over night in distilled water and then subjected to the membrane-forming process.

Record.

April 7, 1905.

Time.	Voltage.	Current.	Resistance.
9.45 A. M.	110.2	0.0008	137750
10.00 "	110.2	0.0007	157430
10.10 "	110.2	0.0006	183680
10.20 "	110.3	0.0006	183830
10.30 "	110.4	0.0006	184000
10.40 "	110.4	0.0006	184000
10.50 "	110.4	0.0006	184000
11.00 "	110.4	0.0006	184000

Manometer No. 4 was used.

Number of calibration units of air reduced to standard conditions = 402.66.

Values Used in the Computations.

0.003665, for temperature coefficient of gases.

0.089826, for the weight of 1 liter of H_2 at Baltimore.

22.488, atmospheres pressure for a gram-molecular weight of H_2 when reduced, at 0°, to a volume of 1 liter.

The cell was set up at 12.10 P. M., April 7.

Initial pressure, uncorrected = 2.3 atmospheres.

Table XIII.—Record of Observations.

(Experiment II. with 0.30 Weight-Normal Solution.)

I. Time.	II. Top of the manometer.	III. Top of mercury column.	IV. Temperature of the solution.	V. Temperature of air in the manometer.	VI. Pressure of liquids in the manometer.	VII. Pressure in atmospheres, uncorrected.	VIII. Calibration units of air in the manometer.	IX. Correction for inversion.	X. Pressure in atmospheres, corrected.	XI. Theoretical gas pressure.	XII. Difference between pressure found and calculated.	XIII. Molecular weight calculated from the equation $M = \frac{W(22.488 + 0.082t)}{p}$
April 7, 1905.												
3.00 P. M.	461.40	560.60				4.72						
5.30 "	466.16	533.74	19°.92	20°.50		6.78						
8.45 "	466.37	523.40	19°.80	19°.90	0.47 Atmosphere.	7.97						
April 8.												
8.40 A. M.	466.80	522.30	18°.30	16°.85		8.18						
12.30 P. M.	467.70	521.40	18°.10	17°.90		8.44						
3.15 "	465.24	518.43	18°.30	18°.55		8.52	51.79		7.24	7.20	0.04	340.3
5.00 "	465.38	518.21	18°.40	18°.80		8.57	51.42		7.30	7.20	0.10	337.6
9.00 "	465.38	518.20	18°.42	18°.50		8.58	51.47		7.29	7.20	0.09	338.1
April 9.												
9.40 A. M.	465.22	518.65	17°.05	15°.90		8.48	51.52		7.13	7.17	—0.04	344.0
12.00 M.	465.11	518.48	16°.90	16°.20		8.49	52.42		7.14	7.16	—0.02	343.3
5.00 P. M.	465.42	518.20	16°.82	16°.74		8.58	52.75		7.25	7.15	0.10	338.1
												340.2

Atmospheric pressure not deducted.

Insufficient for quantitative determination.

0.40 Weight-Normal Solution—Experiment I.

Sugar dissolved in 1,000 grams of water = 136.888 grams.

Specific gravity of the solution at 20° = 1.04846.

Grams of sugar in 1,000 cc. at 20° = 126.28.

Concentration according to the *volume-normal* standard = 0.36886.

Cell B was used. It had previously been set up with a 0.20 weight-normal solution. It was soaked over night in distilled water and subjected to the membrane-forming process.

Record.

April 14, 1905.

Time.	Voltage.	Current.	Resistance.
9.30 A. M.	110.0	0.0030	36667
9.50 "	110.3	0.0023	47957
10.00 "	110.0	0.0022	56000
10.20 "	110.4	0.0023	48000
10.30 "	110.4	0.0023	48000
10.40 "	110.3	0.0023	47957
10.50 "	110.3	0.0024	45960
11.00 "	110.3	0.0025	44130
11.10 "	110.2	0.0026	42385
11.20 "	110.2	0.0027	40816
11.30 "	110.2	0.0027	40816

Manometer No. 3 was used.

Number of calibration units of air = 399.05.

Values Used in the Computations.

0.003665, for temperature coefficient of gases.

0.089826, for weight of 1 liter of H_2 at Baltimore.

22.488, atmospheres pressure for a gram-molecular weight of H_2 when reduced, at 0°, to a volume of 1 liter.

The cell was set up at 12.00 M., April 14, with a 0.40 weight-normal solution containing the usual quantity of ferrocyanide.

Initial pressure = 7.21 atmospheres.

A mistake of 0.1 atmosphere in the measurement of the osmotic pressure of a 0.4 weight-normal solution produces an error of 3.8 units in the estimated molecular weight of cane-sugar.

Table XIV.—Record of Observations.

(Experiment I. with 0.40 Weight-Normal Solution.)

I. Time.	II. Top of manometer.	III. Top of mercury column.	IV. Temperature of the solution.	V. Temperature of air in the manometer.	VI. Pressure of liquids in the manometer.	VII. Pressure in atmospheres, uncorrected.	VIII. Calibration units of air in the manometer.	IX. Correction for inversion.	X. Pressure in atmospheres, corrected.	XI. Theoretical gas pressure.	XII. Difference between pressure found and calculated.	XIII. Molecular weight calculated from the equation $M = \frac{W(22.488 + 0.0824t)}{P}$.
April 14, 1905.												
3.00 P. M.	458.73	504.13	19°.4	19°.25		10.09			9.45	9.61	—0.16	348.1
5.00 "	458.80	503.00	19°.4	19°.41		10.37			9.49	9.61	—0.12	346.8
8.30 "	458.60	502.50	19°.45	19°.64		10.43			9.52	9.62	—0.10	345.7
April 15.												
9.00 A. M.	458.42	501.60	18°.85	18°.50	0.54 Atmosphere.	10.55	40.23		9.61	9.62	—0.01	342.7
12.30 P. M.	458.77	501.56	18°.70	18°.60		10.63	40.07					
3.00 "	458.65	501.37	18°.83	19°.34		10.65	39.97					
5.00 "	458.58	501.23	18°.90	19°.60		10.67	39.61					
8.00 "	458.58	501.12	19°.10	19°.64		10.70						345.8

Atmospheric pressure not deducted.

Insufficient for quantitative determination.

0.40 Weight-Normal Solution—Experiment II.

Sugar dissolved in 1,000 grams of water = 136.888 grams.
Specific gravity of the solution at 20° = 1.04846.
Grams of sugar in 1,000 cc. at 20° = 126.28.
Concentration of the solution according to the *volume-normal* standard = 0.36886.

Cell A was used. It had been previously used in Experiment II., with a 0.20 weight-normal solution. It was soaked in distilled water from 9 A. M. till 11 A. M., April 25, and then subjected to the membrane-forming process.

Record.

April 25, 1905.

Time.	Voltage.	Current.	Resistance.
11.08 A. M.	111.0	0.0020	55500
11.10 "	111.0	0.0015	74000
11.20 "	107.2	0.0012	89330
11.30 "	105.3	0.0011	95730
11.40 "	105.3	0.0011	95730
11.50 "	105.3	0.0011	95730
12.00 M.	105.2	0.0011	95640
12.10 P. M.	105.2	0.0011	95640

Manometer No. 4 was used after the first filling.
Number of calibration units of air = 402.66.

Values Used in the Computations.

0.003665, for temperature coefficient of gases.
0.089826, for weight of 1 liter of H_2 at Baltimore.
22.488, atmospheres pressure for a gram molecular weight of H_2 reduced, at 0°, to a volume of 1 liter.

The cell was set up at 12.30 P. M., April 27, with a 0.40 weight-normal solution containing 0.0846 gram $K_4Fe(CN)_6 . 3H_2O$ per 100 grams of water.
Initial pressure = 3.59 atmospheres.

0.50 Weight-Normal Solution—Experiment I.

Sugar dissolved in 1,000 grams of water = 171.11 grams.
Specific gravity of solution at 20° = 1.05939.
Grams of sugar in 1,000 cc. at 20° = 154.78.

Table XV.—Record of Observations.

(Experiment II. with 0.40 weight-Normal Solution.)

I. Time.	II. Top of manometer.	III. Top of mercury column.	IV. Temperature of the solution.	V. Temperature of air in the manometer.	VI. Pressure of liquids in the manometer.	VII. Pressure in atmospheres, uncorrected.	VIII. Calibration units of air in the manometer.	IX. Correction for inversion.	X. Pressure in atmospheres, corrected.	XI. Theoretical gas pressure.	XII. Difference between pressure found and calculated.	XIII. Molecular weight calculated from the equation $M = \frac{W(22.488 + 0.0824t)}{P}$.
April 27, 1905.												
4.00 P. M.	476.77	530.50				8.45		Insufficient for quantitative determination.	9.70	9.69	0.01	342.0
5.30 "	476.77	524.60	21°.9	21°.6		9.47			9.66	9.68	—0.02	343.1
9.00 "	476.75	519.46	21°.85	21°.7		10.51			9.73	9.68	0.05	340.5
April 28.												
9.00 A. M.	476.81	517.57	21°.2	20°.5	0.49 Atmosphere.	10.99	39.42		9.78	9.68	0.10	338.8
12.30 P. M.	476.75	517.60	20°.9	20°.25		10.98	39.57					341.1
3.00 "	476.79	517.46	20°.84	20°.4		11.02	39.32					
5.00 "	476.90	517.35	20°.8	20°.54		11.08	39.14					

Concentration of the solution according to the *volume-normal* standard = 0.45228.

Cell B was used. It had previously been used with an 0.80 weight-normal solution. After soaking in distilled water for several hours it was subjected to the membrane-forming process.

Record.

April 25, 1905.

Time.	Voltage.	Current.	Resistance.
9.40 A. M.	110	0.0035	31430
9.50 "	110	0.0027	40740
10.00 "	110	0.0023	47825
10.10 "	110	0.0026	42310
10.20 "	110	0.0033	33333
10.30 "	110	0.0038	28956

The cell at this point was again placed in distilled water until 11.15 A. M., when the deposition of the membrane was resumed.

Record.

Time.	Voltage.	Current.	Resistance.
11.25 A. M.	110	0.0038	28950
11.30 "	110	0.0033	33333
11.40 "	110	0.0032	34375
11.45 "	110	0.0032	34375
11.50 "	110	0.0031	35485
12.00 M.	110	0.0031	35485
12.10 P. M.	110	0.0030	36665
12.20 "	110	0.0030	36665
12.30 "	110	0.0030	36665

Manometer No. 4 was used after the first filling.

Number of calibration units of air = 402.66.

Values Used in the Computations.

0.003665, for temperature coefficient of gases.

0.089826, for weight of 1 liter of H_2 at Baltimore.

22.488, atmospheres pressure for 1 gram-molecular weight of H_2 reduced, at 0°, to a volume of 1 liter.

The cell was set up at 1.00 P. M. with a 0.50 weight-normal solution containing the usual quantity of ferrocyanide.

Table XVI.—Record of Observations.

(Experiment I. with a 0.50 Weight-Normal Solution.)

I. Time.	II. Top of manometer.	III. Top of mercury column.	IV. Temperature of the solution.	V. Temperature of air in the manometer.	VI. Pressure of liquids in the manometer.	VII. Pressure in atmospheres, uncorrected.	VIII. Calibration units of air in manometer.	IX. Correction for inversion.	X. Pressure in atmospheres, corrected.	XI. Theoretical gas pressure.	XII. Difference between pressure found and calculated.	XIII. Molecular weight, calculated from the equation $M = \frac{W(22.458 + 0.0824t)}{P}$.
April 25, 1905.												
5.45 P. M.	478.8	514.35	21°.6	21°.5	0.50 Atmosphere.	12.53	32.27	Insufficient for quantitative determination.	11.98	12.10	—0.12	345.8
8.45 "	478.78	512.91	21°.6	21°.7		13.03			11.99	12.10	—0.11	345.4
April 26.												
9.00 A. M.	478.83	512.17	20°.9	20°.3		13.35	32.24		12.00	12.10	—0.10	345.0
12.00 M.	478.78	512.10	20°.8	20°.4		13.37	32.16		12.05	12.10	—0.05	343.7
3.00 P. M.	478.80	512.07	20°.78	20°.7		13.39	32.08		12.05	12.10	—0.05	343.7
5.00 "	478.83	512.05	20°.80	21°.0		13.38	32.08					
8.30 "	478.76	512.00	20°.94	21°.15								
April 27.												
9.00 A. M.	478.63	511.75	20°.80	20°.62		13.40	32.02		12.07	12.10	—0.03	343.1
												344.5

Initial pressure = 10.33 atmospheres.

A mistake of 0.1 atmosphere, in the measurement of the osmotic pressure of a 0.5 weight-normal solution, produces an error of 3.04 units in the estimated molecular weight of cane-sugar.

0.50 Weight-Normal Solution—Experiment II.

Sugar dissolved in 1,000 grams of water = 171.110 grams.

Specific gravity of the solution at 20° = 1.05938.

Grams of sugar in 1,000 cc. at 20° = 154.78.

Concentration of the solution according to the *volume-normal* standard = 0.45228.

Cell A was used. It had previously been used with a 0.60 weight-normal solution. It was soaked over night and then subjected to the membrane-forming process. The circuit was closed at 10.12 A. M., May 5.

Record.

Time.	Voltage.	Current.	Resistance.
10.15 A. M.	110.4	0.0033	33454
10.20 "	110.5	0.0019	58150
10.30 "	110.5	0.0014	79070
10.40 "	110.7	0.0013	85240
10.50 "	110.7	0.0012	92250
11.00 "	110.7	0.0011	100640
11.10 "	110.7	0.0011	100640
11.20 "	110.7	0.0011	100640
11.30 "	110.8	0.0011	100730
11.40 "	110.7	0.0010	110700
11.50 "	110.8	0.0010	110800
12.00 M.	110.8	0.0010	110800

Manometer No. 4 was used.

Number of calibration units of air under normal conditions = 402.66.

Values Used in the Computations.

0.003665, for temperature coefficient of gases.

0.089826, for weight of 1 liter of H_2 at Baltimore.

22.488, atmospheres pressure for a gram-molecular weight of H_2 reduced, at 0°, to a volume of 1 liter.

Table XVII.—Record of Observations.

(Experiment II. with 0.50 Weight-Normal Solution.)

I. Time.	II. Top of the manometer.	III. Top of mercury column.	IV. Temperature of the solution.	V. Temperature of air in the manometer.	VI. Pressure of liquids in the manometer.	VII. Pressure in atmospheres, uncorrected.	VIII. Calibration units of air in the manometer.	IX. Correction for inversion.	X. Pressure in atmospheres, corrected.	XI. Theoretical gas pressure.	XII. Difference between pressure found and calculated.	XIII. Molecular weight calculated from the equation $M = \frac{W(22.488 + 0.0547t)}{P}$.
May 5, 1905.												
3.00 P. M.	469.80	509.36	20°.60	20°.40		11.31			12.16	12.07	0.09	339.7
5.30 "	469.75	506.31	20°.55	20°.25		12.20			12.08	12.07	0.01	342.0
9.00 "	469.86	503.85	20°.50	20°.35		13.09			12.06	12.07	—0.01	342.5
May 6.									12.09	12.07	0.02	341.7
10.00 A. M.	469.78	502.74	20°.10	19°.70	0.50	13.49	31.79		12.20	12.08	0.12	338.9
12.30 P. M.	469.78	502.78	20°.04	19°.70	Atmosphere.	13.48	32.01					
3.00 "	469.70	502.68	20°.02	20°.00		13.48	31.97					
5.00 "	469.70	502.70	20°.10	20°.20		13.48	31.98					
8.30 "	469.72	502.50	20°.30	20°.70		13.56	31.69					
May 17.												
10.15 A. M.	469.69	502.42	20°.80	21°.05		13.58	31.61		12.22	12.10	0.12	338.9
12.30 P. M.	469.65	502.40	20°.90	21°.38		13.57	31.59		12.22	12.10	0.12	339.0
												340.4

Atmospheric pressure not deducted.

Invert sugar found = 0.30 gram in 1,000 grams of water.
Correction at 20° = 0.02 atmosphere.

The cell was set up at 12.30 P. M., May 5, with a 0.50 weight-normal solution containing 0.0846 gram of potassium ferrocyanide per 100 grams of water.

Initial pressure = 8.61 atmospheres.

A mistake of 0.1 atmosphere in the measurement of the osmotic pressure of a 0.50 weight-normal solution produces an error of 3.04 units in the estimated molecular weight of cane-sugar.

0.60 Weight-Normal Solution—Experiment I.

Sugar dissolved in 1,000 grams of water = 205.332 grams.

Specific gravity of the solution at 20° = 1.06986.

Grams of sugar in 1,000 cc. at 20° = 182.24.

Concentration of the solution according to the *volume-normal* standard = 0.53252.

Cell A was used. It had previously been used with a 0.40 weight-normal solution. The cell was soaked in distilled water from April 29 till May 1 and then subjected to the membrane-forming process. The circuit was closed at 10.13 A. M., May 1.

Record.

May 1, 1905.

Time.	Voltage.	Current.	Resistance.
10.15 A. M.	110.0	0.0028	39290
10.20 "	110.0	0.0014	78570
10.30 "	110.0	0.0011	100000
10.40 "	110.0	0.0011	100000
10.50 "	110.0	0.0010	110000
11.00 "	110.0	0.0010	110000
11.10 "	110.0	0.009	122222
11.20 "	110.1	0.009	122330
11.30 "	110.1	0.009	122330
11.40 "	110.1	0.009	122330

Manometer No. 4 was used after first filling.

Number of calibration units of air = 402.66.

Values Used in the Computations.

0.003665, for temperature coefficient of gases.

0.089826, for weight of 1 liter of H_2 at Baltimore.

22.488, atmospheres pressure for a gram-molecular weight of H_2 reduced, at 0°, to a volume of 1 liter.

Table XVIII.—Record of Observations.

(Experiment I. with 0.60 Weight-Normal Solution.)

I. Time.	II. Top of manometer.	III. Top of mercury column.	IV. Temperature of the solution.	V. Temperature of air in the manometer.	VI. Pressure of liquids in the manometer.	VII. Pressure in atmospheres, uncorrected.	VIII. Calibration units of air in the manometer.	IX. Correction for inversion.	X. Pressure in atmospheres, corrected.	XI. Theoretical gas pressure.	XII. Difference between pressure found and calculated.	XIII. Molecular weight calculated from the equation $M = \frac{W(22.485 + 0.0534t)}{P}$
May 1, 1905.												
3.00 P. M.	472.84	544.12	20°.10	22°.00		6.45						
5.00 "	472.08	528.88	20°.10	20°.25		8.00						
8.30 "	471.00	518.15	20°.10	20°.30		9.56						
						Atmospheric pressure not deducted.						
May 2.												
8.15 A. M.	469.35	502.80	19°.20	18°.40		13.30						
12.00 M.	469.22	501.60	19°.06	18°.62		13.69						
3.00 P. M.	469.05	500.76	19°.05	19°.10		14.00						
5.00 "	469.10	500.25	19°.16	19°.50		14.24						
8.30 "	469.00	499.65	19°.30	19°.90		14.47						
May 3.												
9.00 A. M.	468.8	498.21	19°.40	19°.50		15.06						
12.30 P. M.	468.65	497.87	19°.60	20°.10		15.16						
3.00 "	468.72	497.82	19°.86	20°.87		15.26						
5.00 "	468.86	497.60	20°.10	21°.30		15.41						
8.30 "	468.75	497.50	20°.50	21°.90		15.40						
May 4.												
9.00 A. M.	468.72	497.10	21°.21	21°.60	0.51 Atm's-phere.	15.60	27.31		14.23	14.54	—0.31	349.7
12.30 P. M.	468.68	497.00	21°.40	22°.32		15.63	27.19		14.30	14.55	—0.25	348.2
3.30 "	468.86	497.05	21°.80	23°.36		15.70	26.98		14.41	14.57	—0.16	346.0
5.00 "	468.70	497.00	21°.10	23°.80		15.64	27.04		14.38	14.58	—0.20	347.1
												347.7

Invert sugar found = 0.333 gram in 1,000 grams of water.
Correction = 0.02 atmosphere.

The cell was set up at 12 M., May 1, with a 0.60 weight-normal solution.

Initial pressure = 3.98 atmospheres, uncorrected.

A mistake of 0.1 atmosphere in the measurement of the osmotic pressure of a 0.60 weight-normal solution produces an error of 2.52 units in the estimated molecular weight of cane-sugar.

0.60 Weight-Normal Solution—Experiment II.

Sugar dissolved in 1,000 grams of water = 205.332 grams.

Specific gravity of the solution at 20° = 1.06985.

Grams of sugar in 1,000 cc. at 20° = 182.24.

Concentration of the solution according to the *volume-normal* standard = 0.53252.

Cell B was used. It had been previously set up with a weight-normal solution, but when a pressure of 19.5 atmospheres was reached the manometer became loose and the cell was taken down, soaked over night and then subjected to the membrane-forming process. The circuit was closed at 10.30 A. M., May 9.

Record.

May 9, 1905.

Time.	Voltage.	Current.	Resistance.
10.33 A. M.	110.6	0.0071	15580
10.40 "	111.0	0.0037	30000
10.50 "	111.0	0.0031	35810
11.00 "	111.0	0.0030	37000
11.10 "	111.0	0.0028	39640
11.20 "	111.0	0.0027	41110
11.30 "	111.0	0.0026	42690
11.40 "	109.0	0.0024	45420
11.50 "	107.3	0.0023	46650
12.00 M.	110.3	0.0026	42430
12.02 P. M.	110.0	0.0028	35830

The circuit was broken at this point and the cell soaked over night in distilled water. On the following day it was again subjected to the membrane-forming process. The circuit was closed at 11.12 A. M.

Record.

May 10, 1905.

Time.	Voltage.	Current.	Resistance.
11.14 A. M.	110.3	0.0070	15760
11.20 "	110.3	0.0044	25070
11.30 "	110.4	0.0036	30660
11.40 "	110.4	0.0032	34500
11.50 "	110.4	0.0031	35620
12.00 M.	110.4	0.0030	36800
12.10 P. M.	110.4	0.0030	36800
12.20 "	110.4	0.0030	36800

Manometer No. 3 was used after the seventh filling.

Number of calibration units of air in the manometer = 342.13.

Values Used in the Computations.

0.003665, for temperature coefficient of gases.

0.089826, for weight of 1 liter of H_2 at Baltimore.

22.488, atmospheres pressure for a gram-molecular weight of H_2 reduced, at 0°, to a volume of 1 liter.

The cell was set up at 1.00 P. M., May 10, with a 0.60 weight-normal solution containing 0.0846 gram of $K_4Fe(CN)_6 . 3H_2O$ per 100 grams of H_2O.

Initial pressure = 9.06 atmospheres, uncorrected.

A mistake of 0.1 atmosphere in the measurement of the osmotic pressure of a 0.60 weight-normal solution produces an error of 2.52 units in the estimated molecular weight of cane-sugar.

0.70 Weight-Normal Solution—Experiment I.

Sugar dissolved in 1,000 grams of water = 239.554 grams.

Specific gravity of solution at 20° = 1.07993.

Grams of sugar in 1,000 cc. at 20° = 208.69.

Concentration of the solution according to the *volume-normal* standard = 0.60981.

Cell B was used. It was soaked in distilled water over night and subjected to the membrane-forming process.

Table XIX.—Record of Observations.

(Experiment II. with 0.60 Weight-Normal Solution.)

I. Time.	II. Top of manometer.	III. Top of mercury column.	IV. Temperature of the solution.	V. Temperature of air in the manometer.	VI. Pressure of liquids in the manometer.	VII. Pressure in atmospheres, uncorrected.	VIII. Calibration units of air in the manometer.	IX. Correction for inversion.	X. Pressure in atmospheres, corrected.	XI. Theoretical gas pressure.	XII. Difference between pressure found and calculated.	XIII. Molecular weights calculated from the equation $M = \frac{W(22.388 + 0.0834t)}{P}$
May 10, 1905.												
3.00 P. M.	487.49	513.73	22°.9	21°.9		14.51						
5.30 "	487.37	512.80	22°.7	22°.0		14.96						
8.45 "	487.38	512.31	22°.5	22°.0		15.25						
May 11.												
9.30 A. M.	487.35	512.00	21°.6	20°.82		15.41						
1.00 P. M.	487.31	512.11	21°.5	21°.40		15.33						
4.00 "	487.31	512.44	21°.6	22°.00		15.13						
9.30 "	487.26	512.65	21°.9	22°.60		14.98						
May 12.												
9.15 A. M.	487.30	512.44	22°.1	22°.36		15.13						
12.00 M.	487.40	512.50	22°.3	23°.15		15.16						
3.00 P. M.	487.35	512.40	22°.65	24°.20		15.19						
5.00 "	487.35	512.37	23°.00	25°.00		15.20						
8.30 "	487.36	512.33	23°.7	25°.80	0.53 Atmosphere.	15.39	22.84		14.51	14.66	—0.15	345.8
May 13.											—0.19	
9.00 A. M.	487.30	512.00	24°.6	24°.90		15.40	22.75		14.52	14.71		346.7
5.00 P. M.	487.22	511.88	24°.7	25°.05		15.42	22.66		14.37	14.71	—0.34	350.4
9.00 "	487.24	511.95	24°.8	25°.10		15.39	22.75		14.52	14.72	—0.20	346.9
												347.5

Atmospheric pressure not deducted.

Correction at 20° = 0.05 atmosphere.

Invert sugar found = 0.800 gram in 1,000 grams of water.

Record.

April 20, 1905.

Time.	Voltage.	Current.	Resistance.
9.35 A. M.	110.6	0.0027	40970
9.55 "	111.0	0.0015	74000
10.00 "	111.0	0.0014	79280
10.10 "	111.0	0.0013	85380
10.20 "	111.0	0.0012	92500
10.30 "	111.0	0.0012	92500
10.40 "	111.0	0.0011	109000
10.50 "	110.0	0.0011	100000
11.00 "	110.0	0.0011	100000
11.10 "	110.0	0.0011	100000

Manometer No. 4 was used after the first filling.

Number of calibration units reduced to standard conditions = 402.66.

Values Used in the Computations.

0.003665, for temperature coefficient of gases.

0.089826, for weight of 1 liter of H_2 at Baltimore.

22.488, atmospheres pressure for a gram-molecular weight of H_2 reduced, at 0°, to a volume of 1 liter.

The cell was set up at 11.40 A. M., April 20, with a 0.70 weight-normal solution containing the usual amount of potassium ferrocyanide.

Initial pressure = 5.08 atmospheres.

A mistake of 0.1 atmosphere in the measurement of the osmotic pressure of a 0.70 weight-normal solution produces an error of 2.18 units in the estimated molecular weight of cane-sugar.

0.70 Weight-Normal Solution—Experiment II.

Sugar dissolved in 1,000 grams of water = 239.554 grams.

Specific gravity of the solution at 20° = 1.07993.

Grams of sugar in 1,000 cc. at 20 = 208.69.

Concentration of the solution according to the *volume-normal* standard = 0.60981.

Cell B was used. It had previously been used with a 0.60 weight-normal solution. It was soaked from 9.30 A. M. to 3.30

Table XX.—Record of Observations.

(Experiment I. with 0.7o Weight-Normal Solution.)

I. Time.	II. Top of manometer.	III. Top of mercury column.	IV. Temperature of the solution.	V. Temperature of air in the manometer.	VI. Pressure of liquids in the manometer.	VII. Pressure in atmospheres, uncorrected.	VIII. Calibration units of air in the manometer.	IX. Correction for inversion.	X. Pressure in atmospheres, corrected.	XI. Theoretical gas pressure.	XII. Difference between pressure found and calculated.	XIII. Molecular weight calculated from the equation $M = \frac{W(22.488 + 0.0824t)}{P}$.
April 20, 1905.												
3.00 P. M.	478.0	510.8	19°.83	20°.21		13.56						
5.00 "	476.54	506.44	19°.80	20°.3		14.83						
8.30 "	474.70	501.13	19°.9	20°.52		16.75						
April 21.						Atmospheric pressure not determined.						
9.30 A. M.	473.75	497.48	19°.7	20°.66	0.52 Atmosphere.	18.33	22.92	Inv. sugar found = 0.333 Gram in 1.000 Grams of water. Correction at 20° = 0.02 atmosphere. Applied to last two measurements.	17.09	16.87	0.22	338.0
12.30 P. M.	473.35	497.69	19°.81	20°.4		18.11	23.53		16.63	16.88	—0.25	347.4
3.00 "	473.22	497.52	20°.1	21°.4		18.13	23.41		16.72	16.90	—0.18	345.9
5.00 "	473.29	497.56	20°.3	21°.36		18.15	23.39		16.73	16.91	—0.18	346.0
8.30 "	473.30	497.59	20°.6	21°.7		18.11	23.38		16.72	16.93	—0.21	346.5
April 22.												344.1
9.00 A. M.	473.35	497.50	20°.3	19°.8		18.24	23.25		16.82	16.91	—0.19	344.8

P. M. and then subjected to the membrane-forming process. The circuit was closed at 3.39 P. M., May 15.

Record.

May 15, 1905.

Time.	Voltage.	Current.	Resistance.
3.40 P. M.	115.1	0.0160	5714
3.45 "	114.4	0.0050	22880
3.50 "	113.5	0.0043	26400
4.00 "	111.5	0.0040	27880
4.10 "	111.2	0.0042	26475

The current was interrupted and the cell soaked till May 16. The circuit was closed at 10.30 A. M.

Record.

May 16, 1905.

Time.	Voltage.	Current.	Resistance.
10.40 A. M.	114.7	0.0046	24930
10.45 "	114.4	0.0040	28600
10.50 "	114.3	0.0039	29310
11.00 "	113.9	0.0038	29980
11.10 "	113.6	0.0037	30700
11.20 "	113.4	0.0036	31500
11.30 "	113.0	0.0036	31390
11.40 "	112.8	0.0036	31330

Manometer No. 3 was used after the seventh filling.

Number of calibration units of air under standard conditions = 342.13.

Values Used in the Computations.

0.003665, for temperature coefficient of gases.

0.089826, for weight of 1 liter of H_2 at Baltimore.

22.488, atmospheres pressure for a gram-molecular weight of H_2 reduced, at 0°, to a volume of 1 liter.

The cell was set up at 12.30 P. M., May 16, 1905.

Initial pressure = 14.35 atmospheres, uncorrected.

A mistake of 0.1 atmosphere in the measurement of the osmotic pressure of a 0.70 weight-normal solution produces an error of 2.18 units in the estimated molecular weight of cane-sugar.

Table XXI.—Record of Observations.

(Experiment II., with 0.70 Weight-Normal Solution.)

I. Time.	II. Top of manometer.	III. Top of mercury column.	IV. Temperature of the solution.	V. Temperature of air in the manometer.	VI. Pressure of liquids in the manometer.	VII. Pressure in atmospheres, uncorrected.	VIII. Calibration units of air in the manometer.	IX. Correction for inversion.	X. Pressure in atmospheres, corrected.	XI. Theoretical gas pressure.	XII. Difference between pressure found and calculated.	XIII. Molecular weight calculated from the equation $M = \frac{W(22.488 + 0.0824t)}{P}$.
May 16, 1903.												
3.40 P. M.	488.85	510.10	25°.10	24°.70	0.53 Atmosphere.	17.81	19.54	Invert sugar found = 0.250 gram in 1.000 grams of water. Correction at 20° = 0.02 atmosphere.	17.04	17.19	—0.15	345.2
5.50 "	488.85	510.00	25°.00	24°.96		17.89	19.43		17.14	17.18	—0.04	343.1
9.15 "	488.76	510.05	25°.10	25°.40		17.78	19.53		17.05	17.19	—0.14	345.0
May 17.												
9.15 A. M.	488.85	510.08	25°.00	24°.70		17.82	19.52		17.06	17.18	—0.12	344.7
12.00 M.	488.85	510.08	24°.80	24°.30		17.82	19.55		17.03	17.17	—0.14	345.1
3.00 P. M.	488.80	510.02	24°.60	24°.05		17.84	19.55		17.03	17.16	—0.13	344.8
5.00 "	488.77	510.10	24°.50	24°.05		17.74	19.65		16.94	17.16	—0.22	346.5
9.30 "	488.82	510.07	24°.25	23°.75		17.81	19.60		16.98	17.14	—0.16	345.4
May 18.												
9.00 A. M.	488.80	510.03	23°.20	22°.40		17.83	19.67		16.90	17.08	—0.18	345.8
												345.0

0.80 Weight-Normal Solution—Experiment I.

Sugar dissolved in 1,000 grams of water = 273.776 grams.

Specific gravity of the solution at 20° = 1.08960.

Grams of sugar in 1,000 cc. at 20° = 234.17.

Concentration of the solution according to the *volume-normal* standard = 0.68428.

Cell A was used. It had previously been used with a 0.60 weight-normal solution and was soaked in distilled water from 12.00 M. to 3.00 P. M. It was then subjected to the membrane-forming process.

Record.

April 18, 1905.

Time.	Voltage.	Current.	Resistance.
3.05 P. M.	110	0.0025	44000
3.15 "	110	0.0014	78570
3.25 "	110	0.0012	91670
3.35 "	110	0.0011	100000
3.45 "	110	0.0011	100000
3.55 "	110	0.0011	100000
4.05 "	110	0.0011	100000
4.15 "	110	0.0011	100000
4.25 "	110	0.0011	100000
4.35 "	110	0.0011	100000
4.45 "	110	0.0011	100000

Manometer No. 3 was used after the fifth filling.

Number of calibration units reduced to standard conditions = 401.94.

Values Used in the Computations.

0.003665, for temperature coefficient of gases.

0.089826, for weight of 1 liter of H_2 at Baltimore.

22.488, atmospheres pressure for a gram-molecular weight of H_2 when reduced, at 0°, to a volume of 1 liter.

The cell was set up at 3.00 P. M., April 18, with an 0.80 weight-normal solution containing 0.0846 gram $K_4Fe(CN)_6 . 3H_2O$ per 100 grams of water.

Initial pressure = 4.28 atmospheres, uncorrected.

A mistake of 0.1 atmosphere in the measurement of the osmotic pressure of an 0.80 weight-normal solution produces an error of 1.9 units in the estimated molecular weight of cane-sugar.

Table XXII.—Record of Observations.

(Experiment I. with 0.80 Weight-Normal Solution.)

I. Time.	II. Top of manometer.	III. Top of mercury column.	IV. Temperature of the solution.	V. Temperature of air in the manometer.	VI. Pressure of liquids in the manometer.	VII. Pressure in atmospheres, uncorrected.	VIII. Calibration units of air in manometer.	IX. Correction for inversion.	X. Pressure in atmospheres, corrected.	XI. Theoretical gas pressure.	XII. Difference between pressure found and calculated.	XIII. Molecular weight calculated from the equation $M = \frac{W(22.488 + 0.0824t)}{P}$.
April 18, 1895.												
8.15 P. M.	456.33	511.44	19°.6	18°.8								
April 19.												
9.00 A. M.	455.24	477.61	17°.1	15°.74	0.57	19.72						
12.00 M.	455.37	477.47	17°.0	16°.58		20.13						
3.00 P. M.	455.36	477.00	17°.57	18°.36		20.50						
5.00 "	455.38	476.91	17°.90	18°.81		20.60						
8.30 "	455.23	476.80	18°.08	18°.97		20.56						
April 20.												
9.00 A. M.	455.00	476.69	17°.50	16°.96		20.45						
12.00 M.	455.16	476.70	17°.64	18°.00		20.59						
3.00 P. M.	455.15	476.58	18°.15	19°.19		20.69						
5.00 "	455.18	476.59	18°.42	19°.60		20.71						

Atmospheric pressure not deducted.

Atmosphere.

Invert sugar found = 0.340 gram in 1.000 grams water.
Correction at 20° = 0.04 atmosphere.
Applied to last four measurements.

							20.37		19.30	19.15	0.15	339.5
							20.23		19.38	19.17	0.21	338.5
							20.26		19.40	19.18	0.22	338.4
							20.51		19.07	19.14	—0.07	343.5
							20.31		19.27	19.15	0.12	340.1
							20.12		19.50	19.18	0.32	336.7
							20.09		19.53	19.20	0.33	336.6
												339.0

0.80 Weight-Normal Solution—Experiment II.

Sugar dissolved in 1,000 grams of water = 273.776 grams.

Specific gravity of the solution at 20° = 1.08960.

Grams of sugar in 1,000 cc. at 20° = 234.17.

Concentration of the solution according to the *volume-normal* standard = 0.68428.

Cell B was used. It had been previously used with a 0.70 weight-normal solution. It was soaked in distilled water from 9.00 A. M. till 2.45 P. M. and was then subjected to the membrane-forming process.

Record.

April 22, 1905.

Time.	Voltage.	Current.	Resistance.
2.50 P. M.	110.0	0.0037	29730
3.00 "	110.0	0.0028	39290
3.10 "	110.0	0.0022	50000
3.30 "	110.0	0.0027	40740
3.45 "	110.0	0.0036	30555
4.10 "	110.0	0.0037	29730
4.20 "	110.1	0.0034	32385
4.30 "	110.1	0.0032	34410
4.40 "	110.1	0.0031	35520
4.50 "	110.1	0.0030	36700
5.00 "	110.1	0.0030	36700
5.10 "	110.1	0.0030	36700

Manometer No. 4 was used after first filling.

Number of calibration units of air reduced to standard conditions = 402.66.

Values Used in the Computations.

0.003665, for temperature coefficient of gases.

0.089826, for weight of 1 liter of H_2 at Baltimore.

22.488, atmospheres pressure for a gram-molecular weight of H_2 when reduced, at 0°, to a volume of 1 liter.

The cell was set up at 5.45 P. M., April 22, with an 0.80 weight-normal solution containing 0.0846 gram of potassium ferrocyanide per 100 grams of water.

Initial pressure = 3.25 atmospheres, uncorrected.

A mistake of 0.1 atmosphere in the measurement of the osmotic pressure of an 0.80 weight-normal solution produces an error of 1.9 units in the estimated molecular weight of cane-sugar.

Table XXIII.—Record of Observations.

(Experiment II. with 0.80 Weight-Normal Solution.)

I. Time.	II. Top of manometer.	III. Top of mercury column.	IV. Temperature of the solution.	V. Temperature of air in the manometer.	VI. Pressure of liquids in the manometer.	VII. Pressure in atmospheres, uncorrected.	VIII. Calibration units of air in the manometer.	IX. Correction for inversion.	X. Pressure in atmospheres, corrected.	XI. Theoretical gas pressure.	XII. Difference between pressure found and calculated.	XIII. Molecular weight calculated from the equation $M = \frac{W(22.488 + 0.0824t)}{P}$.
April 22, 1895.												
8.30 P. M.	477.15	511.60	22°.7	20°.92		12.92						
April 23.						Atmospheric pressure not deducted.						
10.15 A. M.	474.18	495.30	20°.5	19°.16		20.79						
12.00 M.	474.17	495.20	20°.4	19°.40		20.88						
5.00 P. M.	474.18	495.10	20°.2	19°.85	0.52 Atmosphere.	21.02	20.28	Inv. sugar found = 0.6665 gram in 1,000 grams of water. Correction at 20° = 0.04 atmosphere. Correction applied to last two measurements.	19.37	19.32	0.05	341.4
April 24.												
9.00 A. M.	474.08	494.80	19°.2	18°.40		21.18	20.17		19.48	19.25	0.23	338.3
3.00 P. M.	474.10	494.83	19°.34	19°.92		21.23	20.06		19.55	19.25	0.30	337.3
5.00 "	474.10	494.80	19°.50	20°.40		21.21	20.00		19.61	19.27	0.34	336.4
												338.5

0.89101 Weight-Normal Solution—Experiment 1.

Sugar dissolved in 1,000 grams of water = 304.92 grams.

Specific gravity of the solution at 20° = 1.09840.

Grams of sugar in 1,000 cc. at 20° = 256.665.

Concentration of the solution according to the *volume-normal* standard = 0.75.

Cell A was employed. It had previously been used with a 0.75 volume-normal solution and was soaked over night. It was then subjected to the membrane-forming process.

Record.

March 8, 1905.

Time.	Voltage.	Current.	Resistance.
9.50 A. M.	110.2	0.0023	47910
9.55 "	110.5	0.0018	61390
10.00 "	110.5	0.0015	73670
10.20 "	110.5	0.0011	100450
10.30 "	110.5	0.0010	110500
10.40 "	110.5	0.0009	122780
10.50 "	110.5	0.0009	122780
11.05 "	110.5	0.0008	138120
11.15 "	110.5	0.0008	138120
11.25 "	110.5	0.0008	138120

Manometer No. 3 was used.

Number of calibration units of air under standard conditions = 383.39.

Values Used in the Computations.

0.003665, for temperature coefficient of gases.

0.089826, for weight of 1 liter of H_2 at Baltimore.

22.488, atmospheres pressure for a gram-molecular weight of H_2 when reduced, at 0°, to a volume of 1 liter.

The cell was set up at 11.50 A. M., March 8, with a 0.75 *volume-normal* (= 0.89101 *weight-normal*) solution.

Initial pressure = 8.00 atmospheres, uncorrected.

A mistake of 0.1 atmosphere in the measurement of the osmotic pressure of an 0.89101 weight-normal solution produces an error of 1.87 units in the estimated molecular weight of cane-sugar.

Table XXIV.—Record of Observations.

(Experiment I. with 0.89101 Weight-Normal Solution.)

	I. Time.	II. Top of manometer.	III. Top of mercury column.	IV. Temperature of the solution.	V. Temperature of air in the manometer.	VI. Pressure of liquids in the manometer.	VII. Pressure in atmospheres, uncorrected.	VIII. Calibration units of air in the manometer.	IX. Correction for inversion.	X. Pressure in atmospheres, corrected.	XI. Theoretical gas pressure.	XII. Difference between pressure found and calculated.	XIII. Molecular weight calculated from the equation $M = \frac{W(22.488 + 0.0824t)}{P}$.
March 8, 1905.													
	12.40 P. M.	388.25	441.60										
	12.50 "	388.25	435.00										
	2.30 "	387.80	413.40										
	2.50 "	387.60	412.20	19°.45	18°.30								
	4.00 "	387.40	409.20	19°.70	20°.55								
	5.00 "	387.40	408.40	19°.82	20°.60								
	5.40 "	387.10	408.00	19°.95	20°.60								
	8.30 "	387.00	407.00	20°.20	20°.20								
March 9.													
	8.30 A. M.	386.80	405.80	19°.60	20°.50	0.62 Atmosphere.	22.38	17.74		21.23	21.48	—0.25	346.1
	12.15 P. M.	386.80	405.80	19°.60	19°.80		22.38	17.75		21.21	21.48	—0.27	346.5
	2.30 "	386.65	405.70	19°.80	20°.25		22.32	17.76		21.20	21.49	—0.29	346.9
	5.30 "	386.75	405.75	20°.20	20°.50		22.38	17.70		21.28	21.52	—0.24	346.1
March 10.													
	8.15 A. M.	386.70	405.70	17°.50	17°.25		22.38	17.89		21.01	21.32	—0.31	347.0
													346.5

Atmospheric pressure not deducted.

Correction for inversion = 0.04 atmosphere.
Applied to last reading only.

0.90 Weight-Normal Solution—Experiment I.

Sugar dissolved in 1,000 grams of water = 307.998 grams.

Specific gravity of the solution at 20° = 1.09892.

Grams of sugar in 1,000 cc. at 20° = 258.75.

Concentration of the solution according to the *volume-normal* standard = 0.75610.

Cell B was employed. It had been used previously with an 0.80 weight-normal solution. It was soaked over night in distilled water and then subjected to the membrane-forming process.

Record.

April 30, 1905.

Time.	Voltage.	Current.	Resistance.
10.15 A. M.	110	0.0053	20755
10.30 "	110	0.0033	33333
10.40 "	110	0.0031	35485
10.45 "	110	0.0030	36670
10.50 "	110	0.0030	36670
11.05 "	110	0.0029	37930
11.15 "	110	0.0030	36670

Manometer No. 3 was used after the sixth filling.

Number of calibration units of air under standard conditions = 368.99.

Values Used in the Computations.

0.003665, for temperature coefficient of gases.

0.089826, for weight of 1 liter of H_2 at Baltimore.

22.488, atmospheres pressure for a gram-molecular weight of H_2 when reduced, at 0°, to a volume of 1 liter.

The cell was set up at 1.00 P. M., April 30, with a 0.90 weight-normal solution containing 0.0846 gram $K_4Fe(CN)_6 . 3H_2O$ per 100 grams of H_2O.

Initial pressure = 14.86 atmospheres, uncorrected.

A mistake of 0.1 atmosphere in the measurement of the osmotic pressure of a 0.90 weight-normal solution produces an error of 1.69 units in the estimated molecular weight of cane-sugar.

Table XXV.—Record of Observations.

(Experiment I. with 0.90 Weight-Normal Solution.)

I. Time.	II. Top of manometer.	III. Top of mercury column.	IV. Temperature of the solution.	V. Temperature of air in the manometer.	VI. Pressure of liquids in the manometer.	VII. Pressure in atmospheres, uncorrected.	VIII. Calibration units of air in manometer.	IX. Correction for inversion.	X. Pressure in atmospheres, corrected.	XI. Theoretical gas pressure.	XII. Difference between pressure found and calculated.	XIII. Molecular weight calculated from the equation $M = \frac{W(22.488 + 0.0824f)}{P}$.
April 30, 1905.												
8.15 P. M.	467.10	484.9	21°.2	21°.0	0.57	22.90	16.58		21.82	21.81		342.1
May 1.					Atmosphere.							
9.30 A. M.	467.00	484.65	20°.2	19°.6		23.09	16.60		21.80	21.74	0.06	341.2
1.30 P. M.	467.00	484.66	20°.1	20°.0		23.08	16.56		21.85	21.73	0.12	340.4
3.00 "	466.98	484.67	20°.1	20°.25		23.03	16.58		21.82	21.73	0.09	340.9
5.00 "	467.06	484.65	20°.1	20°.40		23.16	16.48		21.96	21.73	0.23	338.6
8.30 "	466.97	484.68	20°.1	20°.40		23.01	16.59		21.81	21.73	0.08	341.0
May 2.					Atmospheric pressure not deducted.							
8.45 A. M.	467.00	484.60	19°.26	18°.60		23.15	16.59	Invert sugar found = 0.7125 Gram in 1,000 Grams of water.	21.81	21.67	0.14	340.0
12.00 M.	467.00	484.60	19°.10	18°.90		23.15	16.57		21.84	21.65	0.19	339.3
3.00 P. M.	467.00	484.59	19°.10	19°.30		23.16	16.54	Correction at 30° = 0.03 atmosphere.	21.82	21.65	0.17	339.6
5.00 "	467.06	484.60	19°.16	19°.70		23.23	16.47		21.91	21.66	0.25	338.3
												340.1

1.00 Weight-Normal Solution—Experiment I.

Sugar dissolved in 1,000 grams of water = 342.22 grams.

Specific gravity of the solution at 20° = 1.10791.

Grams of sugar in 1,000 cc. at 20° = 282.45

Concentration of the solution according to the *volume-normal* standard = 0.82534.

Cell A was employed. It had previously been used with a normal solution which registered 21.7 atmospheres uncorrected pressure when the manometer was dislodged from the cell. It was then soaked over night and subjected to the membrane-forming process. The circuit was closed at 10.37 A. M.

Record.

May 11, 1905.

Time.	Voltage.	Current.	Resistance.
10.40 A. M.	112.0	0.0021	53300
10.45 "	112.0	0.0016	70010
10.55 "	112.0	0.0015	74670
11.00 "	112.0	0.0013	84200
11.10 "	112.0	0.0011	101800
11.20 "	112.0	0.0011	101800
11.30 "	111.9	0.0010	111900
11.40 "	111.8	0.0010	111800
11.50 "	111.8	0.0010	111800
12.00 M.	110.8	0.00095	116600
12.10 P. M.	110.8	0.00095	116600
12.20 "	110.8	0.00095	116600

Manometer No. 4 was used.

Number of calibration units of air under standard conditions = 402.66.

Values Used in the Computations.

0.003665, for temperature coefficient of gases.

0.089826, for weight of 1 liter of H_2 at Baltimore.

22.488, atmospheres pressure for a gram-molecular weight of H_2 reduced, at 0°, to a volume of 1 liter.

The cell was set up at 1.00 P. M., May 11.

Initial pressure = 6.26 atmospheres, uncorrected.

A mistake of 0.1 atmosphere in the measurement of the osmotic pressure of a weight-normal solution produces an error of 1.52 units in the estimated molecular weight of cane-sugar.

Table XXVI.—Record of Observations.

(Experiment I. with 1.00 Weight-Normal Solution.)

I. Time.	II. Top of manometer.	III. Top of mercury column.	IV. Temperature of the solution.	V. Temperature of air in the manometer.	VI. Pressure of liquids in the manometer.	VII. Pressure in atmospheres, uncorrected.	VIII. Calibration units of air in the manometer.	IX. Correction for inversion.	X. Pressure in atmospheres, corrected.	XI. Theoretical gas pressure.	XII. Difference between pressure found and calculated.	XIII. Molecular weight calculated from the equation $M = \frac{W(22.488 + 0.0824t)}{P}$.
May 11, 1905.												
4.00 P. M.	477.42	504.83	22°.70	21°.30		16.12	15.95		24.76	24.40	0.36	337.3
9.30 "	476.15	497.57	22°.60	22°.60		20.50	15.86		24.90	24.45	0.45	336.2
May 12.						Atmospheric pressure not deducted.						
9.15 A. M.	474.83	492.28	22°.30	22°.26		25.06	15.88	Invert sugar found = 0.745 grain in 1.000 grains of water.	24.87	24.46	0.41	336.6
12.00 M.	474.67	491.87	22°.45	22°.97		25.42	16.01		24.67	24.45	0.22	339.4
3.00 P. M.	474.48	491.39	22°.82	24°.10		25.84	16.01		24.54	24.43	0.11	340.7
5.00 "	474.52	491.27	22°.20	24°.90	0.52 Atmosphere.	26.01		Correction at 20° = 0.03 atmosphere.				338.04
8.30 "	474.40	491.10	22°.90	25°.80		26.16						
May 14.												
11.00 A. M.	474.25	490.85	24°.00	23°.41		26.32						
1.00 P. M.	474.08	490.81	23°.90	23°.30		26.12						
5.30 "	474.00	490.81	23°.60	23°.22		26.00						

1.00 Weight-Normal Solution—Experiment II.

Sugar dissolved in 1,000 grams of water = 342.22 grams.

Specific gravity of the solution at 20° = 1.10791.

Grams of sugar in 1,000 cc. at 20° = 282.45.

Concentration of the solution according to the *volume-normal* standard = 0.82534.

Cell A was employed. It had previously been used with a weight-normal solution. It was soaked in distilled water over night and then subjected to the membrane-forming process. The circuit was closed at 3.26 P. M., May 16.

Record.

May 16, 1905.

Time.	Voltage.	Current.	Resistance.
3.30 P. M.	116.5	0.0031	37580
3.35 "	116.0	0.0020	58000
3.40 "	115.7	0.0017	68060
3.50 "	115.0	0.0015	76670
4.00 "	114.6	0.0013	88150
4.10 "	114.3	0.0012	95250
4.20 "	113.9	0.0012	94920
4.30 "	113.7	0.0012	94750
4.40 "	113.4	0.0012	94500
4.50 "	113.3	0.0012	94420

Manometer No. 4 was used.

Number of calibration units of air under standard conditions = 402.66.

Values Used in the Computations.

0.003665, for temperature coefficient of gases.

0.089826, for weight of 1 liter of H_2 at Baltimore.

22.488, atmospheres pressure for a gram-molecular weight of H_2 reduced, at 0°, to a volume of 1 liter.

The cell was set up at 5.30 P. M., May 16, with a weight-normal solution.

Initial pressure = 11.75 atmospheres, uncorrected.

A mistake of 0.1 atmosphere in the measurement of the osmotic pressure of a 1.00 weight-normal solution produces an error of 1.52 units in the estimated molecular weight of cane-sugar.

Table XXVII.—Record of Observations.
(Experiment II. with 1.00 Weight-Normal Solution.)

I. Time.	II. Top of manometer.	III. Top of mercury column.	IV. Temperature of the solution.	V. Temperature of air in the manometer.	VI. Pressure of liquids in the manometer.	VII. Pressure in atmospheres, uncorrected.	VIII. Calibration units of air in the manometer.	IX. Correction for inversion.	X. Pressure in atmospheres, corrected.	XI. Theoretical gas pressure.	XII. Difference between pressure found and calculated.	XIII. Molecular weight calculated from the equation $M = \frac{W(22.488 + 0.0824t)}{P}$.
May 16, 1895.												
9.15 P. M.	475.65	497.72	25°.30	25°.80		19.91						
May 17.						Atmospheric pressure not deducted.						
9.15 A. M.	473.82	491.57	25°.40	24°.70		24.65						
12.00 M.	473.85	491.10	25°.10	24°.35		25.34						
3.00 P. M.	473.57	490.86	24°.95	24°.10		25.29						
5.00 "	473.62	490.67	24°.70	24°.10		25.62						
9.30 "	473.35	490.23	24°.40	23°.75		25.89						
May 18.												
9.00 A. M.	473.50	490.60	23°.30	22°.45		23.44						
12.30 P. M.	473.15	491.53	23°.10	22°.70		23.82						
3.00 "	473.10	490.09	23°.65	23°.00		25.73						
5.00 "	473.15	490.86	23°.00	23°.10		24.18						
9.30 "	473.20	490.07	23°.00	23°.10	0.52 Atmosphere.	25.90	16.17	Invert sugar found = 0.6665 gram in 1.000 grams of water. Correction at 30° = 0.04 atmosphere.	24.42	24.38	0.04	341.7
May 19.												
9.00 A. M.	473.05	489.93	22°.50	22°.10		25.89	16.22		24.34	24.34	0.00	342.2
12.00 M.	473.20	489.90	22°.40	22°.30		26.16	16.05		24.61	24.33	0.28	338.4
3.00 P. M.	473.08	489.90	22°.40	22°.55		25.98	16.14		24.46	24.33	0.13	340.5
5.30 "	473.10	489.85	22°.40	22°.70		26.09	16.07		24.57	24.33	0.24	339.0
9.30 "	472.95	489.83	22°.50	22°.80		25.89	16.18		24.40	24.34	0.06	341.4
May 20.												
9.30 A. M.	473.00	489.75	21°.90	21°.40		26.08	16.14		24.42	24.29	0.13	340.4
												340.5

1.00 Weight-Normal Solution—Experiment III.

Sugar dissolved in 1,000 grams of water = 342.22 grams.

Specific gravity of the solution at 20° = 1.10791.

Grams of sugar in 1,000 cc. at 20° = 282.45.

Concentration of the solution according to the *volume-normal* standard = 0.82534.

Cell B was employed. It was previously used with a weight-normal solution and afterwards soaked in distilled water from 9.00 A. M. to 3.45 P. M. The circuit was closed at 3.47 P. M.

Record.

May 18, 1905.

Time.	Voltage.	Current.	Resistance.
3.50 P. M.	110.0	0.0075	14640
3.57 "	110.0	0.0056	19640
4.00 "	110.0	0.0043	25580
4.10 "	110.0	0.0038	28290
4.20 "	110.0	0.0034	32360
4.30 "	110.0	0.0032	34380
4.40 "	110.0	0.0032	34380
4.50 "	110.0	0.0032	34380
5.00 "	110.0	0.0031	35480
5.10 "	110.0	0.0031	35480
5.20 "	110.0	0.0038	28950

Manometer No. 3 was used.

Number of calibration units of air under standard conditions = 342.13.

Values Used in the Computations.

0.003665, for temperature coefficient of gases.

0.089826, for weight of 1 liter of H_2 at Baltimore.

22.488, atmospheres pressure for a gram-molecular weight of H_2 reduced, at 0°, to a volume of 1 liter.

The cell was set up at 5.30 P. M., May 18.

Initial pressure, uncorrected = 14.6 atmospheres.

Table XXVIII.—Record of Observations.

(Experiment III. with 1.00 Weight-Normal Solution.)

I. Time.	II. Top of the manometer.	III. Top of mercury column.	IV. Temperature of the solution.	V. Temperature of air in the manometer.	VI. Pressure of liquids in the manometer.	VII. Pressure in atmospheres, uncorrected.	VIII. Calibration units of air in the manometer.	IX. Correction for inversion.	X. Pressure in atmospheres, corrected.	XI. Theoretical gas pressure.	XII. Difference between pressure found and calculated.	XIII. Molecular weight calculated from the equation $M = \frac{W(22.488 + 0.0824t)}{P}$.
May 18, 1905.												
9.30 P. M.	491.30	507.15	23°.30	22°.90		23.69						
May 19.												
9.00 A. M.	491.20	506.72	22°.50	21°.75		24.26						
12.00 M.	491.15	506.90	22°.35	21°.95		23.85						
3.00 P. M.	491.18	506.55	22°.30	22°.30		24.43						
5.30 "	491.24	506.50	22°.35	22°.50		24.60						
May 20.						Atmospheric pressure not deducted.						
9.30 A. M.	491.15	506.10	21°.90	21°.30	0.54 Atmosphere.	25.06	13.88		24.19	24.29	—0.10	343.7
12.00 M.	491.20	506.10	21°.76	21°.40		25.18	13.82		24.29	24.28	0.01	342.1
3.00 P. M.	491.21	506.00	21°.70	21°.60		25.37	13.71		24.49	24.27	0.22	339.2
5.00 "	491.17	506.07	21°.70	21°.80		25.19	13.81		24.27	24.27	0.00	342.3
9.30 "	491.23	506.00	21°.75	21°.90		25.40	13.68		24.51	24.28	0.23	339.0
May 21.												
12.00 M.	491.20	505.89	20°.80	20°.30		25.84	13.77		24.34	24.20	0.14	340.3
												341.1

Invert sugar found = 0.6665 Gram in 1.000 Grams of water.
Correction at 20° = 0.04 atmosphere.

Table XXIX.—Summary of Results.

Weight-normal concentration of solution.	Osmotic pressure, observed. (Atmospheres.)	Gas pressure calculated for same temperature. (Atmospheres.)	Difference between pressure observed and calculated.	Molecular weight calculated from observed pressure.	Molecular weights. Mean values.
		Experiment I.			
0.05	1.23	1.21	0.02	336.3	
	1.23	1.21	0.02	336.1	
	1.28	1.21	0.07	323.3	
	1.31	1.21	0.10	316.1	
	1.34	1.21	0.13	309.4	
	1.28	1.21	0.07	323.9	
	1.26	1.21	0.05	327.5	
	1.28	1.21	0.07	323.8	
	1.30	1.22	0.08	319.7	324.0
		Experiment II.			
	1.16	1.21	—0.05	357.1	
	1.20	1.21	—0.01	345.1	
	1.26	1.21	0.05	328.7	
	1.29	1.21	0.08	320.3	
	1.27	1.21	0.06	326.1	
	1.29	1.21	0.08	320.9	
	1.28	1.21	0.07	323.5	331.7
		Experiment I.			
0.10	2.52	2.41	0.11	327.7	
	2.50	2.41	0.09	330.5	
	2.07	2.37	[—0.30!]	[393.0!]	
	2.22	2.38	—0.11	359.5	
	2.49	2.40	0.09	330.4	337.0
		Experiment II.			
	2.36	2.40	—0.04	348.0	
	2.44	2.40	0.04	336.9	
	2.46	2.40	0.06	334.5	
	2.50	2.40	0.10	329.4	
	2.46	2.40	0.06	333.0	
	2.44	2.40	0.04	336.8	336.6

Weight-normal concentration of solution.	Osmotic pressure, observed. (Atmospheres.)	Gas pressure calculated for same temperature. (Atmospheres.)	Difference between pressure observed and calculated.	Molecular weight calculated from observed pressure.	Molecular weights. Mean values.
		Experiment I.			
0.20	4.75	4.85	—0.10	349.8	
	4.75	4.85	—0.10	349.8	
	4.80	4.85	—0.05	345.6	
	4.77	4.83	—0.06	346.4	
	4.75	4.82	—0.07	347.3	
	4.77	4.82	—0.05	345.9	
	4.78	4.82	—0.04	345.2	347.1
		Experiment II.			
	4.79	4.84	—0.05	346.1	
	4.79	4.84	—0.05	345.9	
	4.82	4.84	—0.02	342.6	
	4.86	4.84	0.02	340.8	
	4.89	4.84	0.05	338.9	
	4.04	4.84	0.01	341.5	342.6
		Experiment I.			
0.25	6.04	6.08	—0.04	344.7	
	6.15	6.09	0.06	339.2	
	6.22	6.11	0.11	336.2	
	6.14	6.11	0.03	340.9	
	6.12	6.12	0.00	342.2	340.6
		Experiment II.			
	5.97	6.08	—0.11	348.5	
	5.96	6.07	—0.11	348.7	
	5.92	6.05	—0.13	349.9	
	6.05	6.06	—0.01	342.9	
	6.00	6.06	—0.06	345.8	347.2
		Experiment I.			
0.30	7.19	7.22	—0.03	343.9	
	7.23	7.22	0.01	342.0	
	7.38	7.23	0.15	345.4	
	7.20	7.24	—0.04	344.1	
	7.19	7.21	—0.02	343.1	
	7.18	7.21	—0.03	343.6	342.0

Weight-normal concentration of solution.	Osmotic pressure, observed. (Atmospheres.)	Gas pressure calculated for same temperature. (Atmospheres.)	Difference between pressure observed and calculated.	Molecular weight calculated from observed pressure.	Molecular weights. Mean values.
		Experiment II.			
	7.24	7.20	0.04	340.3	
	7.30	7.20	0.10	339.6	
	7.29	7.20	0.09	338.1	
	7.13	7.17	—0.04	344.0	
	7.14	7.16	—0.02	343.3	
	7.25	7.15	0.10	338.1	340.2
		Experiment I.			
0.40	9.45	9.61	—0.16	348.1	
	9.49	9.61	—0.12	346.8	
	9.52	9.62	—0.10	345.7	
	9.61	9.62	—0.01	342.7	345.8
		Experiment II.			
	9.70	9.69	0.01	342.0	
	9.66	9.68	—0.02	343.1	
	9.73	9.68	0.05	340.5	
	9.78	9.68	0.10	338.8	341.1
		Experiment I.			
0.50	11.98	12.10	—0.12	345.8	
	11.99	12.10	—0.11	345.4	
	12.00	12.10	—0.10	345.0	
	12.05	12.10	—0.05	343.7	
	12.05	12.10	—0.05	343.7	
	12.07	12.10	—0.03	343.1	344.5
		Experiment II.			
	12.16	12.07	0.09	339.7	
	12.08	12.07	0.01	342.0	
	12.06	12.07	—0.01	342.5	
	12.09	12.07	0.02	341.7	
	12.20	12.08	0.12	338.9	
	12.22	12.10	0.12	338.9	
	12.22	12.10	0.12	339.0	340.4
		Experiment I.			
0.60	14.23	14.54	—0.31	349.7	
	14.30	14.55	—0.25	348.2	
	14.41	14.57	—0.16	346.0	
	14.38	14.58	—0.20	347.1	347.7

Weight-normal concentration of solution.	Osmotic pressure, observed. (Atmospheres.)	Gas pressure calculated for same temperature. (Atmospheres.)	Difference between pressure observed and calculated.	Molecular weight calculated from observed pressure.	Molecular weights. Mean values.
		Experiment II.			
	14.51	14.66	—0.15	345.8	
	14.52	14.71	—0.19	346.7	
	14.37	14.71	—0.34	350.4	
	14.52	14.72	—0.20	346.9	347.5
		Experiment I.			
0.70	17.09	16.87	0.22	338.0	
	16.63	16.88	—0.25	347.4	
	16.72	16.90	—0.18	345.9	
	16.73	16.91	—0.18	346.0	
	16.72	16.93	—0.21	346.5	
	16.82	16.91	—0.19	344.1	344.7
		Experiment II.			
	17.04	17.19	—0.15	345.2	
	17.14	17.18	—0.04	343.1	
	17.05	17.19	—0.14	345.0	
	17.06	17.18	—0.12	344.9	
	17.03	17.17	—0.14	345.1	
	17.03	17.16	—0.13	344.8	
	16.94	17.16	—0.22	346.5	
	16.98	17.14	—0.16	345.4	
	16.90	17.08	—0.18	345.8	345.0
		Experiment I.			
0.80	19.30	19.15	0.15	339.5	
	19.38	19.17	0.21	338.5	
	19.40	19.18	0.22	338.4	
	19.07	19.14	—0.07	343.5	
	19.27	19.15	0.12	340.1	
	19.50	19.18	0.32	336.7	
	19.53	19.20	0.33	336.6	339.0
		Experiment II.			
	19.37	19.32	0.05	341.4	
	19.48	19.25	0.23	338.3	
	19.55	19.25	0.30	337.3	
	19.61	19.37	0.34	336.4	338.5

Weight-normal concentration of solution.	Osmotic pressure, observed. (Atmospheres.)	Gas pressure calculated for same temperature. (Atmospheres.)	Difference between pressure observed and calculated.	Molecular weight calculated from observed pressure.	Molecular weights. Mean values.
0.89101	21.23	21.48	—0.25	346.1	
	21.21	21.48	—0.27	346.5	
	21.20	21.49	—0.29	346.9	
	21.28	21.52	—0.24	346.1	
	21.08	21.32	—0.31	347.0	346.5
0.90	21.82	21.81	0.01	342.1	
	21.80	21.74	0.06	340.4	
	21.85	21.73	0.12	340.9	
	21.82	21.73	0.09	338.6	
	21.96	21.73	0.23	341.0	
	21.81	21.73	0.08	340.0	
	21.81	21.67	0.14	339.3	
	21.84	21.65	0.19	339.6	
	21.82	21.65	0.17	338.3	
	21.91	21.66	0.25	338.3	340.1
		Experiment I.			
1.00	24.76	24.40	0.36	337.3	
	24.90	24.45	0.45	336.2	
	24.87	24.46	0.41	336.6	
	24.67	24.45	0.22	339.4	
	24.54	24.43	0.11	340.7	
	24.79	24.39	0.40	336.7	337.8
		Experiment II.			
	24.42	24.38	0.04	341.7	
	24.34	24.34	0.00	342.2	
	24.61	24.33	0.28	338.4	
	24.46	24.33	0.13	340.5	
	24.57	24.33	0.24	339.0	
	24.40	24.34	0.06	341.4	
	24.42	24.29	0.13	340.4	340.5
		Experiment III.			
	24.19	24.29	—0.10	343.7	
	24.29	24.28	0.01	342.1	
	24.49	24.27	0.22	339.2	
	24.27	24.27	0.00	342.3	
	24.51	24.28	0.23	339.0	
	24.34	24.20	0.14	340.3	341.1

Table XXX.—Mean Molecular Weight for each Concentration.

Concentration.	Molecular weight.
0.05	327.9
0.10	336.8
0.20	344.9
0.25	343.9
0.30	341.1
0.40	343.5
0.50	340.4
0.60	347.7
0.70	344.8
0.80	338.8
0.89101	346.5
0.90	340.1
1.00	339.8
Mean of all determinations,	341.2

It may be questioned whether the pressures which we have measured were *maximum* pressures; whether, in other words, the solutions would not, later, have developed still higher pressures if an opportunity had been given them to do so. We have tested this point on several occasions by allowing cells to remain up from one to two weeks after pressures, such as we have recorded, had been developed and have observed, in all cases, a very slight increase from day to day, but this never exceeded the increase of pressure which was to be expected from the progress of the inversion of the sugar.

The results recorded in this communication appear to the authors to make it probable that the determining factor in osmotic pressure is the numerical ratio existing between the molecules of the dissolved substance and of the solvent, rather than the number of molecules of the dissolved substance which are contained in a unit volume of the solution; further, that the hypothesis of van 't Hoff holds good provided we consider, as the standard quantity of the solvent, that mass of pure water which has the *gas-unit* volume, *i. e.*, 1 liter, at the temperature of maximum density. The results are, perhaps, as concordant as could be expected from a first series of measurements in a field where the progress of the work is hampered by considerable experimental difficulties, but they are by no means the most precise which can be obtained. Certain

sources of error which have, up to the present, beset the work and lessened the precision of the results, can be either altogether eliminated or brought under much better control than hitherto. The measurement of the osmotic pressure of cane-sugar solutions will, therefore, be repeated at an early date, and an attempt will then be made to improve the procedure in various ways, with a view to testing more thoroughly the inferences drawn from the results of the previous work.

The sources of error to which particular attention will be given in the future are: (1) The *thermometer effects*, (2) the uncertainty regarding the true volume of the upper end of the manometer, and (3) the inversion which takes place in the cell.

The source of error which, from the beginning of the work to the end, has given us the most concern is the thermometer effects, *i. e.*, the temporary fluctuations of pressure which follow changes of temperatures, and are due to the expansion or contraction of the liquids in the cell, rather than to actual variations in osmotic pressure. These effects can, of course, be eliminated by maintaining the cell at a constant temperature, or by reducing the rate of change of temperature to a point where the passage of water through the membrane and its distribution through the solution can keep pace with the fluctuations of temperature. We attempted to realize the latter condition by surrounding the cell with non-conducting material, but our efforts were not wholly successful, and we were well aware of the fact that many of the apparent variations in osmotic pressure were, in reality, due to thermometer effects. In the future we shall attempt to maintain constant temperature.

The uncertainty regarding the true volume of that portion of the manometer whose form is affected by the sealing of the instrument does not seriously affect the measurement of the pressure of dilute solutions, but it becomes a matter of great importance when the pressure of a concentrated solution is to be determined.

We are inclined to believe that the inversion of the cane-sugar in the more concentrated solutions was greater than it was, apparently, found to be by the method which was employed to determine it, and when the work is repeated, the

polariscope, instead of Fehling's solution, will be used to measure the inversion which has taken place in the cell.

In his book on Solutions, Ostwald says: "*Dissolved substances exert the same pressure, in the form of osmotic pressure, as they would exert were they gasified, at the same temperature, without change of volume.*" This statement fairly represents, we think, the view generally held respecting the proper magnitude of osmotic pressure, and the known deviations from the rule, as given above, have been regarded as abnormalities, to be reconciled in some way, not yet clear, with the supposed law. The results which we have obtained in the measurement of the osmotic pressure of cane-sugar solutions may be summarized in the following words: *Cane-sugar, dissolved in water, exerts an osmotic pressure equal to that which it would exert if it were gasified at the same temperature and the volume of the gas were reduced to that of the solvent in the pure state.* In other words, dissolved cane-sugar exerts an osmotic pressure throughout the *larger volume of the solution equal to that which, as a gas, it would exert if confined to the smaller volume of the pure solvent.* Stated in this way, all of the thirteen concentrations which have been tested conform to the rule, and no abnormalities appear. Whether the correct standard is the volume of the solvent at the temperature of maximum density, or at the temperature at which the osmotic pressure is measured, will have to be determined by future investigation. The margin of experimental error is still too great to enable us to discriminate between these two possible magnitudes.

The recognition of the fact that the volume relations of solvent and solution play such an important part in the osmotic pressure of cane-sugar solutions led to the suggestion that the so-called *abnormal* freezing-points of the higher concentrations of the same solutions may, in some way, be dependent on, or related to, the degree of the distension of the solvent by the dissolved matter. Accordingly we determined the freezing-points and the density, at zero or slightly below, of all except two of the concentrations, the osmotic pressure of which had been measured. This work is of such recent date that we have not yet been able to develop, except in a superficial manner, the relations which were found to hold between osmotic

pressure on the one side and the depressions of the freezing-point on the other. It is, however, already clear that, in the solution of the problem of *abnormal* freezing-points, some assistance may be expected from a consideration of the relative weights of equal volumes of solvent and solution.

Some of the relations which have appeared will be pointed out:

Let N = the concentration of the solution according to the *weight-normal* standard, *i. e.*, the proportion of a gram-molecular weight of sugar which is dissolved in 1,000 grams of water.

Let D = the density of the solution at its freezing-point, *i.e.*, the relative weights of equal volumes of solution and pure solvent near the temperature of freezing.

Let Δ = the observed depression of the freezing-point.

Let Δ_1 = the calculated depression of the freezing-point.

Then $\Delta_1 = 1.85\ N\ D$ *for all concentrations.*

The verification of the rule will be found in Table XXXI. It will be seen that the observed and calculated depressions of the freezing-points are in close accord for every concentration except possibly two—the 0.50 and 1.00 weight-normal solutions, in which the deviations amount to 0°.011 and 0°.022, respectively. Whether these discrepancies are real, or only the result of experimental errors, we have not yet had time to ascertain The fact, however, that the concentrations on either side of those in question show close conformity to the rule suggests the latter explanation.

The last solution given in the table (the 1.26806 *weight-normal* one) is a *volume-normal* solution, *i. e.*, a solution containing a gram-molecular weight of sugar in a liter volume. The depression of the freezing-point of this solution has been regarded as *abnormal* by the difference between 1°.85 and 2°.66, but it will be noticed that it conforms to the rule with the same degree of precision as the 0.1 weight-normal solution.

Table XXXI.

N.	D.	Δ_1. (1.85 N. D.)	Δ.
0.10	1.0129	0°.187	0°.187
0.20	1.0257	0°.379	0°.373
0.30	1.0380	0°.576	0°.574
0.40	1.0497	0°.777	0°.776
0.50	1.0611	0°.981	0°.970
0.60	1.0717	1°.189	1°.187
0.70	1.0825	1°.401	1°.398
0.80	1.0918	1°.616	1°.612
0.90	1.1016	1°.834	1°.837
1.00	1.1110	2°.060	2°.082
1.26806	1.1340	2°.660	2°.660

A somewhat different aspect of the problem is presented when we consider the apparent influence of the density of the solution upon the equivalence of the freezing-point lowering to osmotic pressure at the temperature of freezing.

If we divide the observed depression of the freezing-point of each weight-normal concentration of solution by the theoretical gas (osmotic) pressure at 0° of the dissolved sugar, we obtain a series of numbers which differ considerably among themselves. This is shown in Table XXXII., in which the weight-normal concentrations of the various solutions occupy the first column, the observed depressions of the freezing-points the second, and the corresponding theoretical gas or osmotic pressures the third. The quotients referred to are given in the fourth column. They are quite irregular in value, but if we divide each of them by the density of the solution near the freezing-point (column 5), we obtain a nearly constant value (column 6), which can be utilized to calculate either osmotic pressure or freezing-point lowering. The mean of all the values so obtained is 0.082.

Table XXXII.

Weight-normal concentration of the solution.	Observed lowering of the freezing-point.	Theoretical gas pressure at 0°.	Observed lowering of the freezing-point divided by the theoretical gas pressure.	Density of the solution at the freezing-point.	Observed lowering of the freezing-point divided by the theoretical gas pressure × density.
0.1	0°.187	2.2488	0.0831	1.0129	0.0818
0.2	0°.373	4.4976	0.0829	1.0257	0.0808
0.3	0°.574	6.7464	0.0895	1.0380	0.0818
0 4	0°.776	8.9952	0.0865	1.0497	0.0821
0.5	0°.969	11.244	0.0862	1.0611	0.0814
0.6	1°.187	13.4928	0.0879	1.0717	0.0820
0.7	1°.398	15.7416	0.0888	1.0825	0.0818
0.8	1°.612	17.9904	0.0896	1.0918	0.0818
0.9	1°.837	20.2392	0.0907	1.1016	0.0828
1.0	2°.082	22.488	0.0926	1.1110	0.0831
1.26806	2°.660	28.765	0.0924	1.1340	0.0822
				Mean value,	0.082

Let D = the density—as compared with water at 0°—of any weight-normal cane-sugar solution near its freezing-point.

Let Δ = the observed lowering of its freezing-point.

Let P = the theoretical osmotic pressure of the solution at 0°.

Then with the aid of the equation $\frac{\Delta}{PD} = 0.082$ it is possible to calculate, very closely, either the osmotic pressure or the depression of the freezing-point of any solution when the other values are known. If the osmotic pressure is known, the depression of the freezing-point will be found by the equation $\Delta = 0.082 \times P \times D$. Or, if the depression of the freezing-point of a cane-sugar solution is known, the osmotic pressure of the solution, at 0°, can be calculated by the equation $P = \frac{\Delta}{0.082 \times D}$. The verification of these equations will be found in Tables XXXIII. and XXXIV.

Table XXXIII.

Concentration.	Osmotic pressure at 0°.	Density of solution at its freezing-point.	Observed lowering of freezing-point.	Osmotic pressure at 0° × density × 0.082.
0.1	2.25	1.0129	0°.187	0.187
0.2	4.50	1.0257	0°.373	0.378
0.3	6.75	1.0380	0°.574	0.574
0.4	9.00	1.0497	0°.776	0.774
0.5	11.24	1.0611	0°.969	0.978
0.6	13.49	1.0717	1°.187	1.185
0.7	15.74	1.0825	1°.398	1.397
0.8	17.99	1.0918	1°.612	1.610
0.9	20.24	1.1016	1°.837	1.828
1.0	22.49	1.1110	2°.082	2.049
1.26806	28.76	1.1340	2°.660	2.674

Table XXXIV.

Concentration.	Observed lowering of freezing-point.	Density of solutions at the freezing-point.	Theoretical gas or osmotic pressure at 0°.	Values of $\frac{\Delta}{0.082D}$ *i. e.*, calculated osmotic pressures.
0.1	0°.187	1.0129	2.25	2.25
0.2	0°.373	1.0257	4.50	4.43
0.3	0°.574	1.0380	6.75	6.74
0.4	0°.776	1.0497	9.00	9.01
0.5	0°.969	1.0611	11.24	11.13
0.6	1°.187	1.0717	13.49	13.50
0.7	1°.398	1.0825	15.74	15.75
0.8	1°.612	1.0918	17.99	18.00
0.9	1°.837	1.1016	20.24	20.33
1.0	2°.082	1.1110	22.49	22.85
1.26806	2°.660	1.1340	28.76	28.82

The conformity to the rule as stated is, in some cases, not as close as could be desired, but the experimental data from which the rule was deduced were gathered rather hastily and have not yet been carefully scrutinized. It is, nevertheless, obvious that the relations here pointed out should be taken into consideration in any attempt to solve the problem of the so-called *abnormal* depressions of the freezing-point. To us it seems probable that at least some of the abnormalities will disappear when the problem is studied from the side of the volume relations of solution and pure solvent; in other words, that, as in the case of osmotic pressure, all concentrations of solution will be found to conform to general rules.

New Semi-Permeable Membranes.

It was stated by one of us, in a preliminary communication,[1] that the electrolytic process is adapted to the deposition, upon or within porous walls, of nearly every kind of precipitate which can be formed from electrolytes in solution and that we were, therefore, in a position to test a variety of insoluble or slightly soluble substances with respect to their possession of the semi-permeable character.

The following substances have thus far been found to exhibit decided osmotic activity, and some of them to a degree which promises future usefulness in the measurement of pressure:

Aluminium hydroxide	Cobalt cobalticyanide
Ferric "	Nickel "
Ferric phosphate	Ferrous "
Uranyl "	Copper "
Cupric "	Zinc "
Uranyl ferrocyanide	Cadmium "
Stannous "	Manganese "
Cadmium "	
Zinc "	
Nickel "	

The compounds mentioned above, as well as several others which appeared to be less promising, were investigated in this laboratory by Messrs. Carver, Coony, and Hall.

Unfortunately, however, the only porous vessels which were available for their work were bottle-shaped cells of 200 cc. capacity, the walls of which were of such open texture and so full of "air blisters" that quantitative measurements of pressure were impossible. They were, therefore, obliged to limit their investigation of these membranes to a determination of the quantities of water which would pass through them in a given time when the cells, filled with solutions of definite concentration, were placed in water; but the activity of osmotic cells in this respect is determined, very largely, by the texture of the cell wall, hence no very definite conclusions could be drawn with regard to the suitability of any of the substances for the quantitative measurement of pressure. Since we have

[1] THIS JOURNAL, 29, 173.

had at our disposal a few cells of excellent character for quantitative work, the investigation of these membranes has been resumed, and each one of them will now be tested by actual use in the measurement of pressure.

JOHNS HOPKINS UNIVERSITY,
May 25, 1905.

REPORT.

A Revision of the Atomic Weights of Sodium and Chlorine.

The work of Stas upon the atomic weights of a number of the elements has been considered one of the classics of chemistry and, in some cases, a variation from the results obtained by him have been, probably without a satisfactory examination, ascribed to errors in the new determinations. In an article under the above title, by Theodore W. Richards and Roger C. Wells,[1] it is pointed out, regretfully, that this reputation is not entirely deserved, as a careful review of several of the determinations made by Stas show sources of serious error.

This revision was undertaken to throw some light upon the unaccountable discrepancy which appeared in the composition of a sample of very pure sodium bromide, as compared with the results obtained by Stas. While, in some cases, the methods of purification used by Stas are open to criticism and there is a strong probability of the presence of slight impurities in the salts used by him, these are not sufficient to explain the discrepancies in the results, they appear to be due to the method of analysis, rather than to the impurity of the material.

Every preparation of sodium chloride made by Stas was fused in contact with platinum and, in a number of cases, also in the presence of ammonium chloride. The authors show that, under such conditions, a noticeable quantity of platinum is always dissolved. Another source of error, for which the proper correction was not made by Stas, was due to the occlusion of gases by the silver and to impurities probably introduced during the process of removing the mother-liquor from the silver buttons. In the present investigation it is, perhaps, unnecessary to say that the weighing and preparation of material was carried out with all possible precaution. The water was most carefully purified, in some instances being condensed and collected entirely in platinum. Special precautions were taken in the preparation of sodium chloride and silver and, in each case, a number of specimens were made from different sources and by different methods. In the majority of instances a pure salt cannot be obtained by precipitating the impurities,

[1] Publication 28, of the Carnegie Institution Reports.

as many assume, but must itself be precipitated or crystallized from the less pure solution. One of the simplest and most satisfactory methods of preparing pure sodium chloride consists in passing hydrochloric acid gas into a strong solution of the salt. A comparison of the material made by this method, with that made by other processes, showed that sodium chloride could be obtained very easily in a pure condition, that water could be expelled from it, by fusion, without loss of halogen and that the salt occludes neither oxygen nor nitrogen.

The silver used in the experiments was obtained from a number of sources, in some cases being first precipitated as the chloride, which was reduced by invert sugar; in others being separated by electrolytic methods and, in still others, by the reduction of the nitrate with ammonium formate. All the specimens of silver were, finally, fused in pure hydrogen and then in a vacuum, to remove occluded matter. Dumas pointed out the necessity of fusing silver in a vacuum to remove occluded oxygen and Stas investigated this source of error and introduced a correction for it; but, in the opinion of the present authors, the correction was not enough, as the silver probably contained as much oxygen as Dumas claimed.

A careful examination of the different methods showed pure lime to be the best support, the amount taken up by the silver being insufficient to affect the results. In testing the solubility of silver chloride and determining its rate of precipitation, the authors selected the method depending upon the intensity of the cloudiness of the opalescent solution, as determined with the nephelometer, an instrument which makes it possible to estimate 1 part of silver chloride in 30,000,000 of water. The solubility was found to vary according to conditions, the presence of sodium nitrate and hydrochloric acid affecting, to a marked extent, the rate at which the intensity of the opalescence increases. The correction for the solubility of silver chloride was applied to the results, although the value was so small as not to affect the third decimal place of the atomic weight of sodium. It is pointed out that Stas' method of dropping solid sodium chloride into a solution of the silver salt is likely to lead to considerable error, because the silver chloride, under these conditions, can occlude large amounts of the salt. They found that, if a moderately concentrated solution of a silver salt is used, or if the precipitate is not washed quickly, the excess of silver salt is enclosed in the silver chloride precipitate, which, upon standing, contracts and envelops the occluded material more securely than at first. Quantitative tests made upon this action of the precipitate showed that,

when solutions not stronger than 0.2 N were used and the precipitates were speedily and thoroughly washed, all the silver nitrate, sodium chloride and sodium nitrate could be removed.

Two methods were used to determine the combining weights of sodium chloride, one depending upon the ratio of the sodium chloride to silver chloride, the other upon the ratio of sodium chloride to silver. Every point was carefully tested and all possible precautions taken to avoid error. By the first method the value found for the atomic weight of sodium was 23.017, as compared with 23.048 obtained by Stas.

The authors point out that, in most of the determinations of the ratios between silver and soluble halogen salts, the method of titration has been used. This method, owing to the fact that it involves no collection and weighing of a precipitate, would be capable of great accuracy if the end point were definite.

Stas attempted to attain an intermediate point, between the limits reached, by titrating to the extreme end with sodium chloride and then running back to the opposite limit with silver nitrate. The results obtained in this way varied considerably, however, owing, as the present investigators show, to the fact that sufficient time was not allowed for the opalescent precipitate to reach a point of equality with the standard. Ten determinations are given, with an extreme variation of 0.004 in the values found. These were selected from a large number as the ones in which every known source of error was avoided and where sufficient time had been allowed for the full development of the opalescence. As 7 different specimens of salt and 3 different preparations of silver were used in the determinations, the limit of purity seems to have been reached. Upon the basis of these results, assuming the atomic weight of silver to be 107.93 and that of chlorine 35.455, the atomic weight of sodium is 23.027.

As the two methods gave values which varied by 0.010, a difference far greater than the sum of the probable experimental errors and which also differed by 0.1 per cent from the value obtained by Stas, a further search for the possible source of error was undertaken.

As Stas' determination of the atomic weight of iodine has been shown to be 0.1 per cent too low, the authors thought it advisable to test the accuracy of his determination of the atomic weight of chlorine, by a series of experiments upon the synthesis of silver chloride. In order to avoid any constant error two methods were used, one consisted in the precipitation, filtration and weighing of the silver chloride formed by dissolving pure silver in pure nitric acid and precipitating with

hydrochloric acid; the other depended on the conversion of silver to silver chloride by the same method, but in a quartz vessel in which the silver chloride could be dried and weighed, without any transfer of material during the entire process. Seven determinations by the former method gave 132.8666, while three by the latter gave 132.8673, the mean value, taking into account the "probable errors," being 132.8668.

As a result of these experiments it could be fairly assumed that 100.000 parts of pure silver yield 132.867 parts of silver chloride. Upon this basis, if the atomic weight of silver is taken as 107.92, the atomic weight of chlorine becomes 35.470, a value 0.095 per cent higher than that obtained by Stas.

Since the atomic weight of chlorine has been the standard to which many others have been referred, a difference in its atomic weight would necessitate a change in many others, in fact all weights depending upon the value of silver, chlorine or sodium would be greatly affected in the second decimal place. In the determination of the ratio of silver chloride to sodium chloride, 100.000 grams of silver chloride were obtained from 40.780 grams of sodium chloride. Using the new value for chlorine, the value for sodium becomes 23.004.

By the other method, where the ratio of silver to silver chloride was determined, the value obtained was 23.007. The authors consider the latter more accurate, because no error is introduced, as in the other method, by the occlusion of sodium nitrate.

The new values, as determined by this investigation, are as follows:

	(Ag = 107.92).	(Ag = 107.930.)
Atomic weight of sodium	23.006	23.008
" " " chlorine	35.470	35.473

It is impossible, in a review, to give more than a general idea of the precautions observed in this research. A large part of the pamphlet is taken up with the minute details which are of fundamental importance in such a revision. After reading the paper, one can hardly avoid feeling that, with our present facilities, the limit of experimental accuracy has been reached and an upward step taken toward the exact atomic weights of sodium and chlorine. J. E. G.

REVIEWS.

EINLEITUNG IN DIE CHEMISCHE KRYSTALLOGRAPHIE. Von P. GROTH. Mit textfiguren. Leipzig: Engelmann. 1904. pp. 80. Price, M4.

The appearance of this little book by Professor Groth, of Munich, is especially timely because of the amount of work

which has been done on the subject during the last decades, since the publication of Fock's work of the same title, in 1888, and Arzruni's more exhaustive work, which appeared as part of Graham-Otto's "Lehrbuch der Chemie," in 1893. The present volume possesses an additional value from the clear style and high standing of the author who, as editor of the *Zeitschrift für Krystallographie und Mineralogie*, has kept closely in touch with the recent publications on the problems of chemical crystallography and has himself practically completed an extensive critical and systematic review of all the investigations which have been made on the relations between crystal forms, the properties of crystalline bodies and their chemical constitution. In the present "Introduction" Professor Groth has brought forward the principal "laws" which these investigations have established or suggested, treating them in five chapters dealing, successively, with the general features of Crystal Structure, Polymorphism, Morphotropism, Isomorphism and Molecular Compounds.

The first chapter, on Crystal Structure, discusses the arrangement of molecules in crystalline bodies, the author favoring Sohncke's theory of interwoven latticeworks of similar form, which unite to form lattices of a common type, in which the individual points are themselves complex. In this chapter well-known facts are reviewed to show that many substances, such as sulphur, may crystallize in different forms and these different modifications are divided into two phases, the polysymmetric and the polymorphic, and tests are given for their distinction. The crystals of those *polysymmetrical* forms, in which the twinning intergrowths are no more observable, are only apparently homogeneous bodies and are distinguished from simple or twinned forms of a lower symmetry solely by those properties which are postulated from the latter by the type of structure. Between the two forms may exist transitions with continuously changing properties and it is not necessary that, for every case, there should be a change from one form to the other at a definite temperature.

The polymorphic modifications represent, on the other hand, practically different states (phases). In the change from one to the other one usually finds a discontinuous change of all the properties, both scalar and vectorial and the alteration occurs at a definite temperature, the alteration-point.

The chapter on Polymorphism limits the concept of polymorphism to such homogeneous, physically different states of a body in which the differences rest in differences of their crystal structure. The polymorphous modifications are assigned, primarily, to the temperature conditions, but the influence of

the presence of crystallizing points of metastable forms is considered and, following both Ostwald and Scham, Groth explains the formations of metastable modifications, such as monoclinic sulphur, instead of the more stable orthorhombic form, as determined by the positions of the alteration-points on the fusion curves. This explanation is also invoked in the discussion of monotropic and enantiotropic forms. In conclusion, it is recognized that the facts at hand do not warrant the statement of any general law for the relations between the crystal structure and the polymorphic modifications, although the isolated cases carefully studied hold out much hope for fruitful investigations in the future.

The chapter on Morphotropism deals with the dependence of the crystal structure on the chemical constitution of the body. The author here, after describing the changes produced by substitutions as in the nature of homogeneous deformations of the crystal structure, explains the manner of measuring these modifications and gives the morphotropic influence of elements and radicals. The influence on the crystal structure of substituting CH_3, Cl, Br, I, NO_2 or OH for H, is summarized in the following law :

"The alteration, in many cases, occurs appreciably in definite directions, so that one may infer from them something regarding the arrangement of the atoms in the regular structure.

"The type and amount of the deformation depends upon the nature of the entering parts (atoms or atomic groups) and upon the crystal structure of the bodies in which the substitution takes place.

"1. On the position of the substituted hydrogen atoms in the chemical molecule—thence isomeric bodies possess different crystal structures.

"2. On the size of the chemical molecule, since the alteration of the crystal structure, in general, is less, the more complicated the compound is, in which the occurring chemical change takes place."

The chapter on Isomorphism includes discussion of (A) the harmony of crystal structure in chemical compounds of analogous constitution ; (B) the relations between crystals and solutions of isomorphous bodies ; (C) Isomorphous Mixtures.

Under this head a few leading investigations, notably the well-known studies of Tutton on the sulphates and selenates of potassium, rubidium and caesium, are reviewed and isomorphic bodies are practically defined as those which show very close agreement in crystal structure because of the similarity of morphotropic effects of related elements. As thus defined there is, manifestly, no sharp limit between isomorphous

and morphotropic bodies, but such a definition unites the two types of structural change together and is in harmony with the looser and more general use of the term isomorphism.

Under the second head is briefly discussed the well-known ability of isomorphous substances to grow in solutions of their isomorphs, or to serve as centers of crystallization. These instances are regarded, not as isomorphous growths, as they are often loosely described, but rather as cases of episomorphism and an evidence of the probable isomorphic relations of the substances involved. Isomorphism is really based upon the close similarity of crystal structures and the ability to form homogeneous mixed crystals, in all proportions of the end members.

Under the third head, Isomorphous Mixtures, the author considers the relations between isomorphism and mixed crystals. The discussion seems to involve differences in conception and definition as to what is isomorphism. Van 't Hoff assumes that the mixed crystals are solid solutions in which the laws for gases apply, others hold that the end members are present as individual molecules. Retgers emphasized the complete continuity of the series of mixed crystals, from end member to end member, in which the constituents crystallized in all proportions, the properties of the mixed crystals forming continuous functions of the composition; Roozeboom and Brune lay stress on the fusion curves, which might apply equally well to certain mixed crystals of non-isomorphous end members. Groth, on the other hand, would include among the "true isomorphous mixtures all those cases in which two substances, which possess no completely analogous chemical composition but a very close affinity of crystal structure, form continuous series of homogeneous mixed crystals, as for example, the triclinic feldspars." This last view would involve an analogy to the polysymmetrical bodies in which we have stable crystals composed of regularly alternating lamellae of sub-microscopic size, which possess the same type of crystal structure.

The discussion of isomorphous mixtures leads, naturally, to that of molecular compounds, but here the treatment seems less satisfactory, chiefly because the relations of the crystal structures of so-called molecular compounds with those of their components have been little investigated. Among the molecular compounds are the racemic salts, consisting of varying amounts of antipodal components leading to active and inactive crystals. The author, following Pasteur, holds that both optical antipodes of an optically active compound possess enantiomorphic crystal structures and, further, that this is a direct consequence of the enantiomorphism of their chemical mole-

cules. Pseudoracemic bodies, with crystal properties, specific gravity and fusion-point similar to those of their component antipodes, are regarded as sub-microscopic intergrowths of the active components. These may be distinguished from true racemates by a comparative study of their solubility and fusion values with those of the active components. E. B. M.

ROCKS, ROCK-WEATHERING AND SOILS. By GEORGE P. MERRILL. New York: Macmillan Company. 1904. pp. 411, illustrated. Price, $4.00.

The appearance of the second edition of this rather unique volume by Professor Merrill is, in itself, an evidence of the value of the work. The book, which has for its theme the changes and processes by which the solid rocks of the earth's crust pass to the more or less incoherent covering of soils, is, at once, a compilation of many scattered data and an original contribution to the subject of rock-weathering. The somewhat unusual scope and the original methods of attack place the book in a field by itself. Other works dealing with rocks or soils as central themes give many facts regarding the passages from the former to the latter, but the author makes the transitions the central point.

The book is divided into five parts dealing, successively, with the constituents and properties of rocks, their kinds, the weathering which they undergo, the methods of removal and redistribution of rock débris and the resulting vegetable or mantle of unconsolidated materials.

In the first two parts the discussion is clear and conservative, well illustrated and well arranged. There is, however, some question as to the propriety of devoting nearly half the entire work to this more distinctly petrographical part, since the matter is available in other works and many of the minerals and rocks described are scarcely, if at all, mentioned in the later portions of the volume.

The third part of the book, dealing with the weathering of the rocks, containing as it does a discussion of the principles, manifestations and conditions of weathering, is the best of the whole. Most of the material is new and much of it is the result of the author's own investigations. In this portion of the book are many new analyses of rocks and especially analyses of the same rock in different stages of degeneration. The manner of computing the relative loss of constituents, during rock-weathering, is of especial interest. It is assumed, with reason, that alumina and ferric iron are the most stable and that relatively little of these constituents has been removed. On this basis the relative removal of the remaining constituents has been computed. The most important changes indicated

are hydration, a loss in silica, a relatively greater loss in lime, magnesia and the alkalies and an apparent gain in alumina and, occasionally, iron. The cumulative effect is a decided loss of materials, which may amount to 50 per cent of siliceous rocks and even 99 per cent, in extreme cases, of calcareous rocks.

The discussion of transportation and redistribution occupies but a few pages, although containing many facts regarding the different agents at work.

The treatment of the Regiolith, including the discussion of soils is good, though, possibly, somewhat disappointing to certain soil investigators.

The book, as a whole, is an excellent piece of work, well thought out, clearly expressed, admirably illustrated and well published. It is, however, to be regretted that the press of other duties did not permit the author to bring the subject up to date in this later edition. E. B. M.

THE CHEMICAL SYNTHESIS OF VITAL PRODUCTS AND THE INTER-RELATIONS BETWEEN ORGANIC COMPOUNDS. By RAPHAEL MELDOLA-F.R.S., V.P.C.S., F.I.C., Professor of Chemistry in the City and Guild, of London Technical College, Finsbury; Member of the Faculty of Science, University of London, etc. Vol. I.: Hydrocarbons, Alcohols and Phenols, Aldehydes, Ketones, Carbohydrates and Glucosides, Sulphur and Cyanogen Compounds, Camphor and Terpenes, Coloring Matters of the Flavone Group. London: Edward Arnold. 1904. pp. 338. Price, 21 shillings, net.

The author has imposed upon himself a most laborious task in the preparation of this work. It is a reference book in which are catalogued only those organic substances that have been produced synthetically and which occur in living things, whether animal or vegetable, or are produced by the growth of microörganisms. No theories are considered and the author limits himself to the statement of facts. The occurrence and methods of synthesis are tabulated under each compound, together with copious references to the very scattered literature on this subject.

A few quotations from the introduction will make clear the scope and aim of the work. "It is in no sense to be regarded as a critical work and my whole object has been to bring practical workers, whether chemists, physiologists or technologists into communication with the authorities quoted." The term "vital product" is used by the author in a broad sense and "has been enlarged so as to include every atomic complex which, without unduly straining the facts, there is reason for believing to be present in the products resulting from vital synthesis, the other condition for insuring inclusion in this work being, of course, that the complex has been synthesized in the laboratory." Thus salicylic acid and methyl alcohol

are included in this work, on account of the occurrence of methyl salicylate, although neither have been found to occur in the free state.

The author points out that pyrogenic syntheses and those accomplished by the use of violent reagents do not resemble, in any way, the vital syntheses and are, therefore, from a biochemical point of view, of little interest. Hence, the ordinary chemical classification and arrangement are laid aside and the substances which are genetically related are brought together, regardless of the type of the compounds. "The treatment of organic chemistry in this work has accordingly been entirely subordinated to the biochemical view of the subject." The author states that he is "not without hope that this work may be found of service as a step towards the foundation of a more exact science of biochemistry" and "that the present résumé will materially assist any future discussion of the problems of biochemistry." These are very high hopes for a work of this character. It will, undoubtedly, prove of much value as a book of reference and should be within reach of all who are working in this field. Only a more extended usage can determine how thoroughly and carefully the work of compilation has been done. The second volume, which will complete the work, is now in preparation. A. S. L.

THE FOLLIES OF SCIENCE AT THE COURT OF RUDOLPH II. By HENRY CARRINGTON BOLTON. Milwaukee: Pharmaceutical Review Publishing Company. 1904. pp. 217.

In this book an attempt has been made to give some account of the character of the scientific atmosphere pervading the Court of Rudolph II, Emperor of Germany. To the chemist it will be of special interest for the reason that it deals, to a considerable extent, with alchemy. Alchemy has been called one of the six follies of science, the others being the quadrature of the circle, the multiplication of the cube, perpetual motion, judicial astrology and magic. The author says: "Alchemy, after astrology, probably contributed more directly than any other of the six follies of science towards the advancement of the genuine science associated with it."

The book will be found interesting not only by the chemist but by the general reader, as it is not rendered incomprehensible by the use of technical language. I. R.